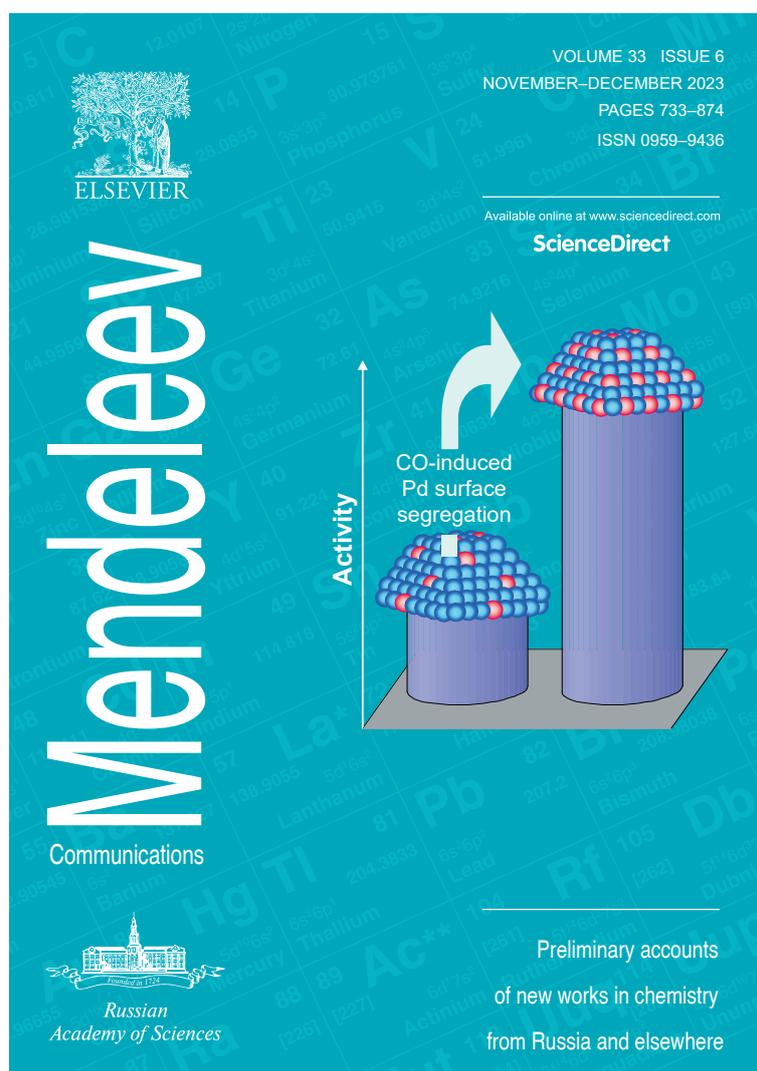


Provided for non-commercial research and educational use only.
Not for reproduction or distribution or commercial use.



This article was originally published in a journal published by Elsevier in cooperation with Mendeleev Communications, and the attached copy is provided for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues that you know, and providing a copy to your institution's administrator.

All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>

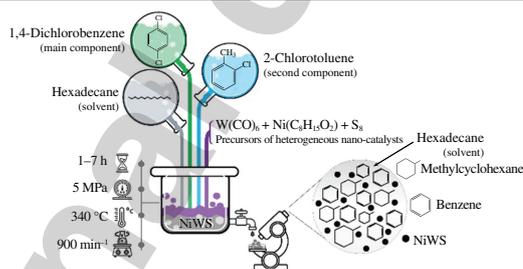
Hydrodechlorination of a two-component mixture of chloroaromatic compounds in the presence of an unsupported sulfide catalyst

Eduard G. Dzhabarov,* Natalya N. Petrukhina and Elena M. Zakharyan

 A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: dzhabarov@ips.ac.ru

DOI: 10.1016/j.mencom.2023.10.033

The effects of reaction time on the conversion of 2-chlorotoluene and heptene-1 and two-component systems were determined. The hydrodechlorination of 1,4-dichlorobenzene was accelerated in the presence of heptene-1. The high activity of an unsupported NiWS catalyst was shown in the hydrodechlorination and hydrogenation of a 1,4-dichlorobenzene–2-chlorotoluene (heptene-1) mixture.



Keywords: hydrodechlorination, hydrogenation, unsupported sulfide catalysts, chloroaromatic compounds, 1,4-dichlorobenzene, 2-chlorotoluene.

There is growing concern^{1–3} about the need to recycle chlorine-containing wastes including polyvinyl chloride (PVC).^{4,5} Thermal processing (pyrolysis), which produces a liquid (pyrolysis oil) containing various chloroaromatic and unsaturated cyclic and non-cyclic compounds, can be used for recycling PVC waste.⁶ The variety of organochlorine compounds in the pyrolysis oil is determined by the processing of waste based on chlorine-containing feedstock (processing of mixtures of polymer waste or chlorine-containing polymers with hydrocarbon fractions or other municipal waste).⁷ The presence of even a small quantity of chlorine-containing compounds in pyrolysis oil/waste does not allow the pyrolysis products to be used as fuel or petrochemical feedstock with a concentration of chlorine-containing compounds in liquid products not exceeding 10 ppm.⁸

Catalysts based on platinum group metals (Pd, Pt, and Rh)^{9–13} and supported catalysts based on transition metals (Ni, W, Mo, and Co)^{14–17} were studied in the hydrodechlorination of chlorinated organic compounds. However, the first group of catalysts suffered severe deactivation due to a high chlorine content in feedstock, whereas the second group was deactivated by the destruction of the support due to the interaction with HCl. We found that unsupported sulfide catalysts based on Ni, W, Mo, and Co showed a higher activity and stability in the hydrodechlorination of 1,4-dichlorobenzene in *n*-hexadecane as a model mixture in comparison with those of similar industrial supported catalysts NBC-A (NiW), AKM (CoMo), and AGKD-400 (NiMo). The morphology and phase composition were also established.¹⁸ The active NiWS phase was formed during the hydrodechlorination; Ni was a promoter, and W was the main metal. However, there are no published data on a combination of the hydrodechlorination and hydrogenation of two-component systems on unsupported transition metal sulfide catalysts. Hence, the aim of this work was to study the hydrogenation of an olefin and an aromatic compound in the presence of chlorinated compounds on *in situ* formed unsupported NiWS sulfide catalysts using a two-

component mixture of 1,4-dichlorobenzene and heptene-1 and the hydrodechlorination of a two-component mixture of organochlorine compounds (1,4-dichlorobenzene and 2-chlorotoluene) on the *in situ* formed NiWS catalyst.

The hydrodechlorination of 1,4-dichlorobenzene on the NiWS catalyst proceeded with the formation of benzene, and cyclohexane was not detected in the system.¹⁸

To investigate the possibility of the hydrogenation of unsaturated compounds (olefins, aromatics) in the presence of organochlorine components, we studied the combined hydrogenation of heptene-1 and hydrodechlorination of 1,4-dichlorobenzene.[†] The exhaustive hydrogenation of heptene-1 took 3 h [Figure 1(a)]. When 1,4-dichlorobenzene was added at the same concentration to a model mixture of heptene-1 in hexadecane, the olefin conversion in hydrogenation did not decrease; that is, the hydrogenation was not affected by chlorine-containing components [Figures 1(a),(b),(e)]. On the other hand, the presence of heptene-1 in the 1,4-dichlorobenzene–*n*-hexadecane system accelerated the hydrodechlorination (synergetic effect): in the hydrodechlorination of 1,4-dichlorobenzene in the one-component system, the yield of chlorobenzene after 4 h of reaction was 50%, whereas the yield of chlorobenzene did not exceed 4% in the two-component system [Figures 1(b),(e)].

[†] Nickel 2-ethylhexanoate ($\geq 78\%$, Sigma-Aldrich) and $W(CO)_6$ (JSC ‘Redkinskiy pilot plant’) were used as precursors of heterogeneous nano-catalysts. The substrate was 1,4-dichlorobenzene ($\geq 99\%$, Sigma-Aldrich), 2-chlorotoluene (98%, Acros Organics), heptene-1 ($\geq 99\%$, JSC Component-Reactiv). The sulfidation agent was elemental sulfur (ChemMED LLC). *n*-Hexadecane ($\geq 98\%$, JSC Component-Reactiv) was used as a solvent. The catalysts were synthesized *in situ* in the reaction medium during hydrodechlorination and/or hydrogenation in a batch type reactor with constant stirring at 340 °C; the H_2 pressure was 6 MPa ($\geq 98\%$, Air Liquide), 1–7 h.¹⁸

The products were analyzed by gas chromatography on a Crystalux-4000M chromatograph (NPF Meta-Chrom Ltd.) with an Optima 1 capillary column (30 m \times 0.32 mm \times 0.50 μ m).

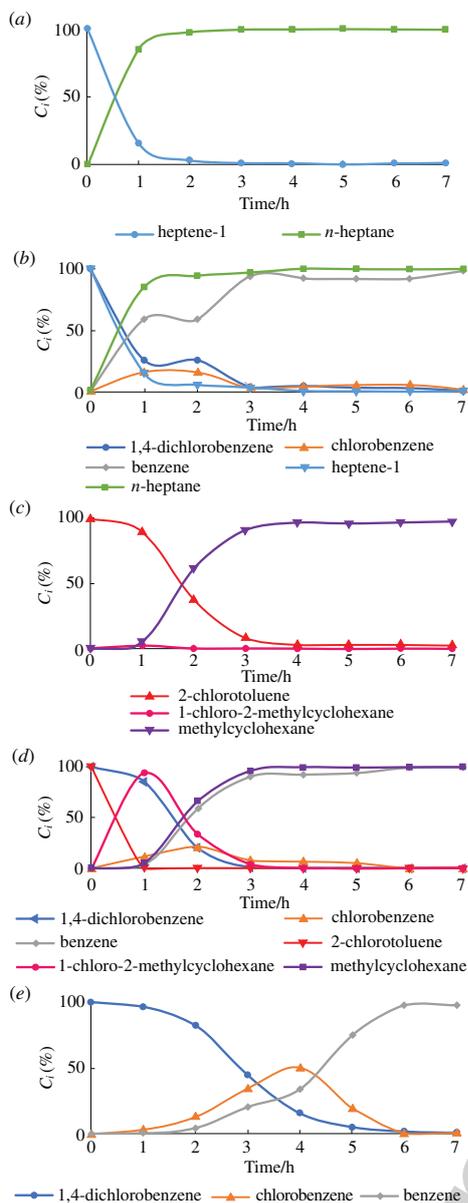


Figure 1 Time dependences of (a) hydrogenation of heptene-1, (b) hydrogenation-hydrodechlorination of 1,4-dichlorobenzene and heptene-1, (c) hydrodechlorination of 2-chlorotoluene, (d) hydrodechlorination of 1,4-dichlorobenzene and 2-chlorotoluene, and (e) hydrodechlorination of 1,4-dichlorobenzene in the presence of NiWS, where C_i is the component concentration in the mixture. Conditions: H_2 , pressure 6 MPa; temperature, 340 °C; 10% solution of 1,4-dichlorobenzene : 2-chlorotoluene (heptene-1) = 1 : 1 in *n*-hexadecane; W/feedstock = 1/80 (mol mol⁻¹) in the one-component system; W/1,4-dichlorobenzene = 1/40 (mol mol⁻¹) in the two-component system.

The hydrodechlorination and hydrogenation of a one-component model mixture of 2-chlorotoluene in hexadecane proceeded predominantly with the formation of the final product (the selectivity for methylcyclohexane was 91.5–97.8%) [Figure 1(c)]. The presence of another chlorine-containing component (1,4-dichlorobenzene) in a mixture of 2-chlorotoluene in hexadecane caused two consecutive processes: 1-chloro-2-methylcyclohexane was formed with 100% selectivity in the first hour of the reaction (hydrogenation) followed by the hydrodechlorination and hydrogenation to methylcyclohexane [Figures 1(d),(e)]. The hydrodechlorination of 1,4-dichlorobenzene was not slowed down in the presence of 2-chlorotoluene due to a sufficient number of available active sites of the unsupported NiWS catalyst.

In the hydrodechlorination of two-component systems (1,4-dichlorobenzene/heptene-1 and 1,4-dichlorobenzene/2-chlorotoluene), a chlorobenzene intermediate formed from

1,4-dichlorobenzene was not affected by the second component in the mixture [Figures 1(b),(d)]. In the presence of an olefin, a sharp decrease in the concentration of 1,4-dichlorobenzene (25.5%, 1 h) was observed with the selective formation of benzene [Figure 1(b)], whereas 2-chlorotoluene prevented the substitution of Cl groups (85%, 1 h) [Figure 1(d)].

In conclusion, the unsupported NiWS catalyst showed a high activity: the exhaustive hydrogenation of heptene-1 was achieved in 3 h with the hydrodechlorination of 2-chlorotoluene in 4 h. In the simultaneous hydrogenation of heptene-1 and hydrodechlorination of 1,4-dichlorobenzene, a synergetic effect was observed: in the presence of the olefin, the substitution for Cl with benzene formation was accelerated. The hydrodechlorination of a mixture of 1,4-dichlorobenzene and 2-chlorotoluene was as fast as the hydrodechlorination of 1,4-dichlorobenzene due to the presence and availability of a plethora of active sites of the unsupported NiWS catalyst. Unlike 1,4-dichlorobenzene, 2-chlorotoluene first underwent hydrogenation to 1-chloro-2-methylcyclohexane due to a methyl substituent in the *ortho* position and then hydrodechlorination to methylcyclohexane.

This study was performed within the framework of a state assignment of the Institute of Petrochemical Synthesis of the Russian Academy of Sciences.

References

- E. M. Zakharyan, N. N. Petrukhina and A. L. Maksimov, *Russ. J. Appl. Chem.*, 2020, **93**, 1271 (*Zh. Prikl. Khim.*, 2020, **93**, 1218).
- E. M. Zakharyan, N. N. Petrukhina, E. G. Dzhabarov and A. L. Maksimov, *Russ. J. Appl. Chem.*, 2020, **93**, 1445 (*Zh. Prikl. Khim.*, 2020, **93**, 1370).
- G. McKay, *Chem. Eng. J.*, 2002, **86**, 343.
- L. Lu, W. Li, Y. Cheng and M. Liu, *Waste Manage.*, 2023, **166**, 245.
- O. V. Arzhakova, M. S. Arzhakov, E. R. Badamshina, E. B. Bryuzgina, E. V. Bryuzgin, A. V. Bystrova, G. V. Vaganov, V. V. Vasilevskaya, A. Yu. Vdovichenko, M. O. Gallyamov, R. A. Gumerov, A. L. Didenko, V. V. Zefirov, S. V. Karpov, P. V. Komarov, V. G. Kulichikhin, S. A. Kurochkin, S. V. Larin, A. Ya. Malkin, S. A. Milenin, A. M. Muzafarov, V. S. Molchanov, A. V. Navrotsky, I. A. Novakov, E. F. Panarin, I. G. Panova, I. I. Potemkin, V. M. Svetlichny, N. G. Sedush, O. A. Serenko, S. A. Uspenskii, O. E. Philippova, A. R. Khokhlov, S. N. Chvalun, S. S. Sheiko, A. V. Shibaev, I. V. Elmanovich, V. E. Yudin, A. V. Yakimansky and A. A. Yaroslavov, *Russ. Chem. Rev.*, 2022, **91**, RCR5062.
- J. Pan, H. Jiang, T. Qing, J. Zhang and K. Tian, *Chemosphere*, 2021, **284**, 131348.
- P. Das and P. Tiwari, *Resour. Conserv. Recycl.*, 2018, **128**, 69.
- T. Bhaskar, M. A. Uddin, K. Murai, J. Kaneko, K. Hamano, T. Kusaba, A. Muto and Y. Sakata, *J. Anal. Appl. Pyrolysis*, 2003, **70**, 579.
- M. A. Álvarez-Montero, L. M. Gómez-Sainero, J. Juan-Juan, A. Linares-Solano and J. J. Rodríguez, *Chem. Eng. J.*, 2010, **162**, 599.
- A. Arevalo-Bastante, M. A. Álvarez-Montero, J. Bedia, L. M. Gómez-Sainero and J. J. Rodríguez, *Appl. Catal., B*, 2015, **179**, 551.
- L. M. Gómez-Sainero, J. Palomar, S. Omar, C. Fernández, J. Bedia, A. Álvarez-Montero and J. J. Rodríguez, *Catal. Today*, 2018, **310**, 75.
- M. A. Álvarez-Montero, L. M. Gómez-Sainero, A. Mayoral, I. Diaz, R. T. Baker and J. J. Rodríguez, *J. Catal.*, 2011, **279**, 389.
- M. Bonarowska, Z. Kaszkur, L. Kępiński and Z. Karpiński, *Appl. Catal., B*, 2010, **99**, 248.
- E. Puello-Polo, Y. Diaz and J. L. Brito, *Catal. Commun.*, 2017, **99**, 89.
- W. Piechocki, G. Gryglewicz and S. Gryglewicz, *J. Hazard. Mater.*, 2009, **163**, 1397.
- B. F. Hagh and D. T. Allen, *AIChE J.*, 1990, **36**, 773.
- D. A. Ryaboshapka, E. S. Lokteva, E. V. Golubina, A. N. Kharlanov, K. I. Maslakov, A. O. Kamaev, A. V. Shumyantsev, I. A. Lipatova and E. I. Shkol'nikov, *Kinet. Catal.*, 2021, **62**, 127 (*Kinet. Catal.*, 2021, **62**, 55).
- E. G. Dzhabarov and N. N. Petrukhina, *Pet. Chem.*, 2022, **62**, 1334 (*Nanogeterogenyi Kataliz*, 2022, **7**, 1).

Received: 17th July 2023; Com. 23/7213