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Transfer hydrodechlorination of chlorobenzene over Ni–Mo sulfide system and effect of HCl neutralizer

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Table S1. Data on the percentage composition of the reaction mixture at various points in time. Transfer hydrodechlorination of PhCl **1** using CaO as HCl absorber at different temperatures: 250 °C; 275 °C; 300 °C.

T = 250 °C				
Time, min	Composition, mol.%			
	PhCl **1**	PhH **2**	PhPr^i **3**	PhPr **4**
0	97	4	0	0
20	74	22	3	3
40	57	33	5	4
60	42	45	6	7
90	26	53	8	9
120	15	67	9	10
180	4	74	11	11
240	2	75	12	12
T = 275 °C				
Time, min	Composition, mol.%			
	PhCl **1**	PhH **2**	PhPr^i **3**	PhPr **4**
0	81	12	2	2
20	55	33	4.5	5
40	23	54	8	9
60	10	61	9	11
90	2	67	9	12
120	0	67	10	12
180	0	67	10	13
240	0	70	10	15
T = 300 °C				
Time, min	Composition, mol.%			
	PhCl **1**	PhH **2**	PhPr^i **3**	PhPr **4**
0	69	18	2	0
20	22	46	8	8
40	6	63	9	10
60	1	67	10	11
90	0	67	10	12
120	0	67	10	13
180	0	67	11	15
240	0	67	12	16

Table S2. Data on the percentage composition of the reaction mixture. Transfer hydrodechlorination of PhCl **1** at 275 °C using different HCl absorbers: $CaCO_3$, K_2CO_3; $NaHCO_3$, and Et_3N.

$CaCO_3$ as HCl absorber				
Time, min	Composition, mol.%			
	PhCl **1**	PhH **2**	PhPr^i **3**	PhPr **4**
0	79	10	2	2
20	54	28	5	5
40	38	38	6	7
60	28	44	7	8
90	20	52	8	9
120	16	57	8	9
180	11	59	9	10
240	9	61	9	10
K_2CO_3 as HCl absorber				
Time, min	Composition, mol.%			
	PhCl **1**	PhH **2**	PhPr^i **3**	PhPr **4**
0	90	7	0	0
20	64	27	1	1
40	47	40	2	3
60	29	52	3	4
90	19	60	3	5
120	8	65	4	6
180	2	69	4	7
240	1	74	5	8
$NaHCO_3$ as HCl absorber				
Time, min	Composition, mol.%			
	PhCl **1**	PhH **3**	PhPr^i **3**	PhPr **4**
0	78	14	2	2
20	49	39	5	5
40	24	55	7	8
60	12	67	8	9
90	3	69	9	11
120	1	69	9	11
180	0	69	10	11
240	0	70	10	12
Et_3N as HCl absorber				
Time, min	Composition, mol.%			
	PhCl **1**	PhH **3**	PhPr^i **3**	PhPr **4**
0	92	5	0	0
20	78	15	0	0
40	65	23	0	0
60	60	34	0	0
90	52	42	0	0
120	44	49	0	0
180	36	56	0	0
240	28	63	0	0

Table S3. Selectivity of PhCl **1** transfer hydrodechlorination using CaO as HCl absorber at the end of the process at different temperatures: 250 °C; 275 °C; 300 °C.

Process temperature, °C	Selectivity, %			
	PhCl **1**	PhH **2**	$PhPr^i$ **3**	PhPr **4**
250	2	74	12	12
275	0	74	10	16
300	0	71	13	17

Table S4. Selectivity of PhCl **1** transfer hydrodechlorination using different HCl absorber at the end of the process.

HCl absorber	Selectivity, %			
	PhCl **1**	PhH **2**	$PhPr^i$ **3**	PhPr **4**
$CaCO_3$	10	69	10	11
K_2CO_3	1	84	6	9
$NaHCO_3$	0	76	11	13
Et_3N	31	69	0	0

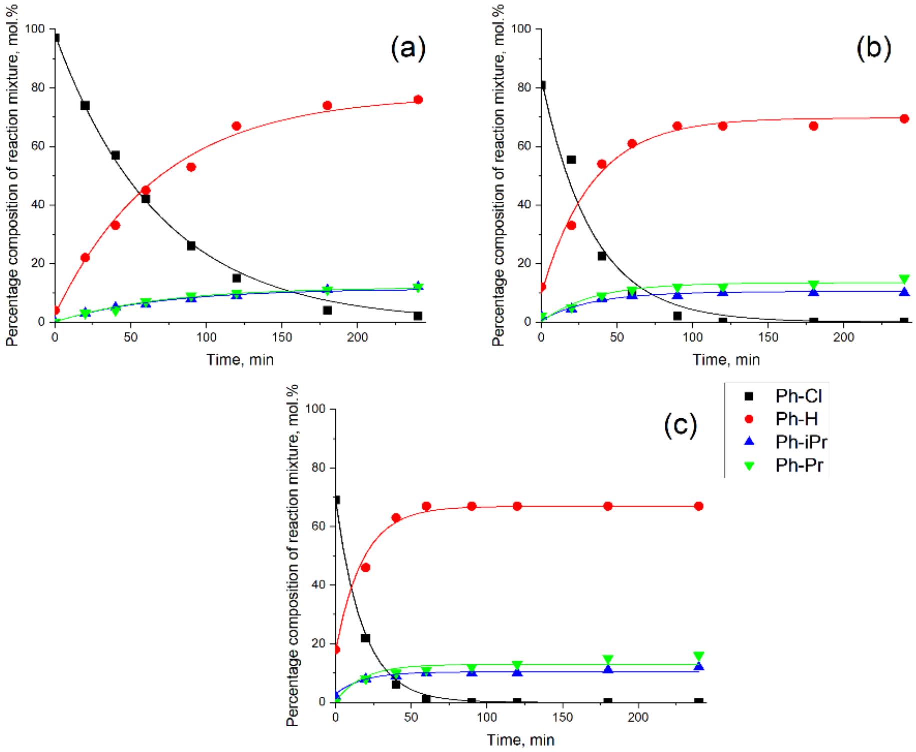

Figure S1. Percentage composition of the reaction mixtures as functions of time. Transfer hydrodechlorination of PhCl **1** using CaO as HCl neutralizer at different temperatures: (*a*) – 250 °C; (*b*) – 275 °C; (*c*) – 300 °C. The points are experimental data and the lines are data calculated from the quasi-first order kinetic model.

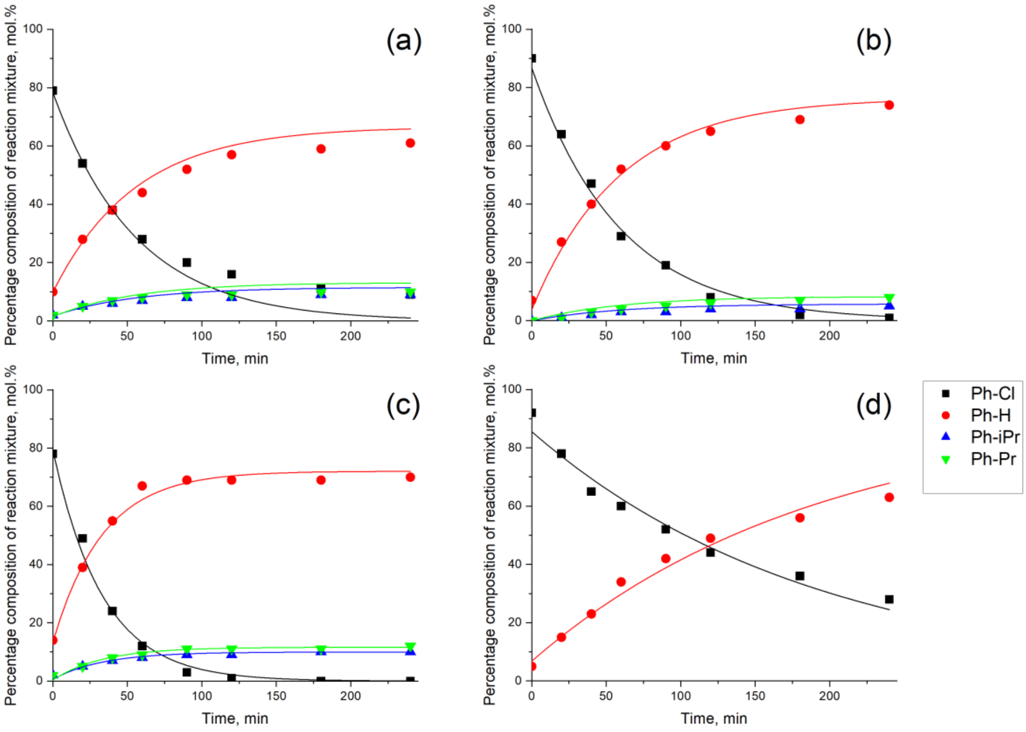

Figure S2. Percentage composition of the reaction mixtures as functions of time. Transfer hydrodechlorination of PhCl at 275 °C using different HCl neutralizers: (*a*) – $CaCO_3$, (*b*) – K_2CO_3; (*c*) - $NaHCO_3$; (*d*) – Et_3N. The points are experimental data and the lines are data calculated from the quasi-first order kinetic model.

Materials and methods

Reagents

The following reagents have been used: chlorobenzene (99.8 %, Soyuzkhimprom, Russia), dodecane (≥99 %, Sigma-Aldrich), 2-propanol (≥99.5 %, SigmaAldrich), nickel hydroxide (99 % extra, Acros Organics), methanol (J.T. Barker, HPLC Gradient Grade), benzene (99 %, SigmaAldrich), CaO (97.5 %, Soyuzkhimprom, Russia), $CaCO_3$ (99 %, Soyuzkhimprom, Russia), NaHCO3 (99 %, Soyuzkhimprom, Russia), K_2CO_3 (98 %, Soyuzkhimprom, Russia), Et3N (99.5 %, SigmaAldrich), γ-Al_2O_3 (99 %, NPK-Syntez, Russia), ammonium heptamolybdate (99 %, Baltic Enterprise Ltd., Russia).

Catalyst synthesis

The Ni3Mo13 catalyst was synthesized by pore volume impregnation method (Salomatina *et al*., 2022). The impregnating solution was prepared by sequential dissolution of citric acid, nickel hydroxide, and ammonium heptamolybdate in distilled water under vigorous stirring at 50 °C. Concentrations of components in impregnating solution were chosen to obtain 3 wt % of NiO and 13 wt % of MoO_3 in the unsulfided sample. The nominal metal content was 8.7 wt % of Mo and 2.4 wt % of Ni, in the sulfided catalyst. After complete dissolution, the mixture obtained was used for impregnation of the support. Catalyst was dried at 120 °C for 2 h after impregnation and then it has been sulfided in H_2S flow before catalytic tests. For this a catalyst sample in the form of fraction 0.5−0.25 mm was placed in the quartz reactor and sulfided at atmospheric pressure and stepwise temperature rise: the first temperature stage was at 220 °C and the second was at 400 °C (Vatutina *et al.*, 2021).

Catalyst characterization

XRD

The XRD measurements were carried out using a STOE STADI MP X-ray diffractometer (STOE, Germany) equipped with a MYTHEN2 1K detector. The XRD patterns were measured using the Mo Kα radiation (λ = 0.7093 Å) in the 2θ range of 3°− 32° with a step of 0.015° and accumulation time of 3 s at each point. The XRD phase analysis was performed using the ICDD PDF-4 + database. The TOPAS software was used for the analysis of peak profiles and for the Rietveld refinement. The mean size of coherently scattering regions or crystallites (D_{XRD}) was estimated by the line broadening analysis according to the Scherrer equation. The instrumental broadening was determined from the XRD pattern of a standard reference material (silicon).

N_2 adsorption

An ASAP-2400 automated volumetric adsorption analyzer (Micromeritics Instrument. Corp., USA) was used to determine the texture characteristics of the catalysts. The samples were dried under vacuum at room temperature and then replaced into a special cell under inert (argon) atmosphere. After degassing at 300 °C and residual pressure of 0.13 Pa for 7 h, adsorption isotherms were measured at the liquid nitrogen temperature (− 196 °C). The surface area (S_{BET}) of the samples was determined by the Brunauer–Emmett–Teller method.

Batch experiments

The catalyst (~0.44 g for the experiments) was loaded into a batch reactor (Hastelloy c276, 285 ml). Then, a solution containing 0.88 g of chlorobenzene (7.82 mmol), ~0.145 g of dodecane (internal standard), 120 ml of 2-propanol, and 30 mmol-equivalents of base was added to the reactor. After that, the reactor was purged with argon under stirring (with a mechanical agitator MagneDrive®). The reactor was closed and heated to the required temperature (250 – 300°C). The reaction was carried out at a constant temperature with permanent stirring at 800 rpm. The self pressure of the reaction mixture achieved 7.1–11.0 MPa. During the experiment, the reaction mixture was periodically sampled for the analysis. To calculate the conversion of chlorobenzene and selectivities for benzene and alkylbenzene, the following equations were used:

$$Conversion = \frac{|Chlorobenzene|_{in} - |Chlorobenzene|_{fin}}{|Chlorobenzene|_{in}} \cdot 100\%$$

$$Benzene\ selectivity = \frac{|Benzene|}{\sum|All\ aromatic\ products|} \cdot 100\%$$

$$Alkylbenzene\ selectivity = \frac{\sum|Alkylbenzene|}{\sum|All\ aromatic\ products|} \cdot 100\%$$

Product analysis

The liquid samples were analyzed using a Shimadzu GCMS–QP2010 SE chromato-mass spectrometer equipped with an autosampler and with a GsBP-INOWAX capillary chromatographic column (crosslinked polyethylene glycol, a length of 30 m, an internal diameter of 0.32 mm, and a stationary phase thickness of 0.25 μm). The temperature mode of column conditioning was as follows: 40 °C for 2 min, heating to 110 ◦C at a rate of 9 K min^{-1}, and then heating to 250 °C at a rate of 15 K min^{-1}. The evaporator temperature was 250 °C, split 1:15, and helium was used as a carrier gas. A flow rate of the carrier gas was 1.8 ml/min. The products were identified using a peak retention time and mass spectra, which were compared with the data from the NIST and Wiley7 electronic mass spectral libraries or, in some cases, with corresponding data on pure compounds. The conversion of chlorobenzene and the yield of products were evaluated using dodecane as an internal standard.

Results and discussion

Catalyst properties

The diffraction pattern of the sulfidated Ni3Mo13 catalyst is shown in Figure S3. The most intense reflections belong to the nanocrystalline metastable phase γ-Al_2O_3 (PDF# 000-029-0063) with lattice parameters $a = b = c = 7.915(2)$ Å. The average D_{XRD} size is $D = 6.5$ nm. Also in the diffraction pattern there are additional strongly broadened maxima in the region of angles 4.5-8°, 13.7-17° and 24.5-28° 2θ, indicating the formation of a poorly crystallized, highly dispersed MoS_2 phase (PDF#00-037-1492, $a = b = 3.161$ Å, $c = 12.299$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$). The strongest reflection [002] is strongly broadened by 8° 2θ from the MoS_2 phase. These features indicate the ultra-small size of the coherent scattering region in the crystallographic direction [001], which is the direction of stacking of S-Mo-S packets in the layered structure of MoS_2. Estimated by the broadening of the reflex [002], the average size of the crystallites in the [001] direction is 2.5, which corresponds to two S-Mo-S packets in the layered structure of MoS_2. The lateral size of the crystallites (the size along the packages), estimated from the broadening of the reflex [110], is about 3 nm. Thus, it can be concluded that the formation of MoS_2 crystallites of anisotropic shape in the form of plates with a small number of packages in the direction of laying layers.

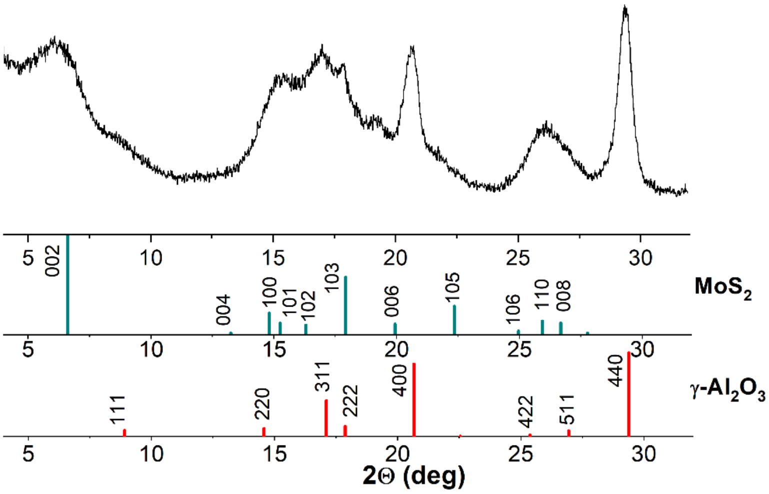

Figure S3. Experimental XRD patterns for Ni3Mo13 sulfide catalyst.

Ni3Mo13 sulfide catalyst has a developed specific surface area of more than 200 m^2 g^{-1}. The given textural characteristics of the catalyst (see Table S5) are typical for catalysts for refining petroleum fractions. It should be noted that this article demonstrates the first use of catalysts based on molybdenum sulfides used in hydrogen transfer processes.

Table S5. Textural characteristics of the Ni3Mo13 sulfide catalyst: S_{BET} - specific surface area; V_{pores} - specific pore volume; R_{pores} - average pore size.

Sample	S_{BET}/m^2 g^{-1}	V_{pores}/cm^3 g^{-1}	R_{pores}/nm
Ni3Mo13	294	0.14	2.5