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

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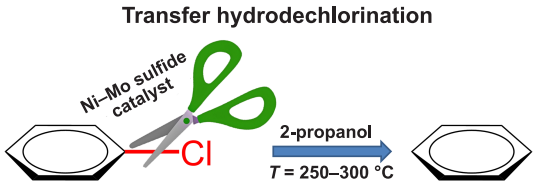
Catalytic transfer hydrodechlorination of chlorobenzene using 2-propanol as the hydrogen donor and a mixed Ni–Mo sulfide phase deposited on alumina as the catalyst is studied at temperatures 250–300 °C. When triethylamine is applied as the HCl neutralizer, benzene is the only product, whereas with inorganic bases (iso)propylbenzenes are also formed.



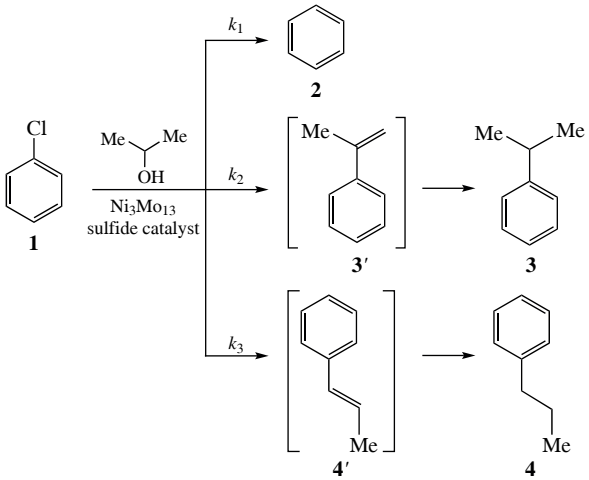
Keywords: transfer hydrodechlorination, nickel–molybdenum sulfide system, 2-propanol, chlorobenzene, benzene.

Catalytic hydrodechlorination can be considered a 'green' method for the removal of organic chlorine from chlorine-containing oils, including hydrogenation with cleavage of the C–Cl bond.[1] Gaseous H_2 is the most commonly used hydrogen donor,[2–4] but formic acid[5,6] and lower alcohols[7] have also been successfully used in model hydrodechlorination processes. Palladium-containing metal systems are currently among the most studied for hydrodechlorination processes,[8,9] and such systems are also applicable when using alcohols as hydrogen donors.[10,11] It should be noted that despite the 'mild' dechlorination conditions,[12] the price of these catalysts limits their use in large-scale processes.

The use of alcohols in the hydrogen transfer reaction as an alternative to traditional hydrogenation processes is a promising direction.[13] The use of 2-propanol shows high efficiency in the catalytic hydrogenolysis of C–O and C–N bonds in some aromatic compounds.[14] Alcohols as hydrogen donors also allow the removal of oxygen from model bio-oil compounds.[15–18] The hydrogen transfer reaction can also be used to remove oxygen from biomass.[19] The use of different catalysts for the hydrogen transfer reaction is reviewed.[20]

In this work, an original approach is proposed for the use of molybdenum sulfide-based catalysts in the dechlorination of chlorobenzene (PhCl) **1** using 2-propanol as the hydrogen donor (Scheme 1). The effect of the HCl neutralizer nature on the rate and selectivity of the process has also been studied. The use of CaO as an HCl neutralizer in hydrodechlorination of organochlorine compounds is a fairly common approach. In the initial stage, experiments on transfer hydrodechlorination of PhCl were carried out at temperatures of 250, 275 and 300 °C. Data on the composition of the reaction mixture during the transfer hydrodechlorination of PhCl are shown in Table S1 of the Online Supplementary Materials, the main products having been benzene **2**, isopropylbenzene (cumene) **3** and *n*-propylbenzene **4**. At the initial stage of dechlorination there were observed trace amounts of products with C=C double bonds such as 2-phenylpropene **3′** and 1-phenylpropene **4′**, apparent precursors for compounds **3** and **4**, respectively. Based on the data obtained (see Table S1), we proposed a scheme for sequential transformations of PhCl **1** (see Scheme 1), which made it possible to conduct kinetic modeling and to calculate the observed rate constants. In order to study the effect of the nature of the HCl neutralizer on the rate and selectivity of the hydrodechlorination process, a temperature of 275 °C was chosen because, on the one hand, at this temperature it is possible to achieve complete conversion of PhCl **1** and, on the other hand, to estimate more accurately the rate constants of the processes (see Online Supplementary Materials, Figure S1).

The conversion rate constants for transfer hydrodechlorination of PhCl **1** using different HCl neutralizers $CaCO_3$, K_2CO_3, $NaHCO_3$ and Et_3N are given in Table 1. Data on the percentage composition of the reaction mixture are presented in Table S2. When K_2CO_3, $NaHCO_3$ and Et_3N are used as HCl neutralizers, the kinetic curves are fairly well described by the quasi-first order kinetic model, but when $CaCO_3$ is used, there is a significant deviation of the experimental data from the quasi-first order kinetic model (see Figure S2). Probably, this deviation when using $CaCO_3$ is due to the mechanism of catalytic



Scheme 1

Table 1 Rate constants for PhCl transformations determined by the least-squares method using the obtained analytical solution and experimental data on PhCl conversion under different conditions.[a]

T/°C	HCl neutralizer	k_1/s^{-1}	k_2/s^{-1}	k_3/s^{-1}
250	CaO	1.83 ± 0.03	0.28 ± 0.02	0.29 ± 0.02
275	CaO	3.58 ± 0.15	0.58 ± 0.06	0.79 ± 0.07
300	CaO	6.55 ± 0.23	1.00 ± 0.08	1.67 ± 0.09
275	$CaCO_3$	not modeled	not modeled	not modeled
275	K_2CO_3	2.37 ± 0.06	0.19 ± 0.03	0.27 ± 0.03
275	$NaHCO_3$	3.69 ± 0.10	0.58 ± 0.05	0.71 ± 0.05
275	Et_3N	0.87 ± 0.03	–	–

[a] k_1, k_2 and k_3 are the quasi-first order rate constants.

conversion, perhaps the low solubility of $CaCO_3$, unlike other neutralizers, does not provide a sufficient basic medium in the system that would affect the process rate. It should be noted that the conversion rate constants k_1, k_2 and k_3 during the hydrodechlorination process at a temperature of 275 °C using CaO and $NaHCO_3$ as HCl neutralizers are almost identical, which is also confirmed by the close selectivity values of the processes (Tables S3 and S4). When K_2CO_3 is used, the conversion rate constants k_1, k_2 and k_3 are lower than those in cases of CaO and $NaHCO_3$, but the proportion of alkylated benzene products with K_2CO_3 is lower than that with CaO and $NaHCO_3$ (see Tables S3 and S4). A significant change in the composition of the hydrodechlorination products is observed when the organic base Et_3N is used as the HCl neutralizer. Thus, in addition to the slowing down of the dechlorination process (see Table 1), the arene alkylation does not occur, and so in this case the only product is PhH **2** (Figure S2, part *d*). The acidic centers of the alumina used as a support for the catalyst probably play an important role in the alkylation of the aromatic ring (the Friedel–Crafts reaction), and so when Et_3N is used, these centers can be completely blocked.

In summary, the use of different basic HCl neutralizers (CaO, $CaCO_3$, K_2CO_3, $NaHCO_3$ and Et_3N) in the transfer hydrodechlorination of PhCl in a 2-propanol medium catalyzed by a Ni–Mo sulfide catalyst leads to both a change in the selectivity of the process and a change in the dechlorination rate of PhCl: $CaO \approx NaHCO_3 < K_2CO_3 < CaCO_3 < Et_3N$. Thus, when inorganic HCl neutralizers are used, reductive substitution products such as (iso)propylbenzenes **3** and **4** are observed, whereas in case of Et_3N the only product is benzene **2**.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7630.

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