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The complexes of copper with grafted ionic liquids in the environmentally important processes

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ABSTRACT

The complexes of copper (II) chloride with quaternary ammonium salts grafted on various mineral supports (the modifications of SiO_2 – KSK, silochrome, Perlkat) are highly active in two environmentally important processes: the reaction of carbon tetrachloride with alkanes and the oxidative coupling of thiols. The effectiveness of the catalysts depends on the transition metal, the ionic liquid, and the support nature. In CCl_4 transformations, the highest activity is shown by the complexes with alkylamines derivatives grafted on silica with wide pores. In case of thiol oxidation, complexes with heterocycles derivatives grafted on Perlkat with narrow pores are most active. The effectiveness of the CCl_4 transformations catalysts increases upon the addition of alcohol to the reaction mixture.

1. Introduction

In recent years, ionic liquids (IL) have been widely used as media for performing chemical processes and as components of catalytic compositions. A promising trend is the development of heterogeneous metal complex catalysts based on IL grafted on mineral supports [1–3]. The immobilized catalysts were found to be active in various processes: e.g., hydroformylation [4–6], hydrogenation [7,8], hydrodechlorination [9], methanol carbonylation [10], Friedel–Crafts reaction [11,12], oxidation of phenols [13], alcohols [14] and thiophene [15], Heck reaction [16]. At the same time there are very few radical reactions that can be catalyzed by such complexes. Kharasch addition of CCl_4 to alkenes is the example of such process [17,18]. We present two other radical processes that can be catalyzed by immobilized copper complexes with ionic liquids. The first one is the liquid-phase oxidation of thiols with air oxygen, leading to the formation of disulfides:

$$4RSH + O_2 = 2RSSR + 2H_2O$$

and the liquid phase interaction between alkanes and carbon tetrachloride:

$$RH + CCl_4 \rightarrow RCl + CHCl_3$$

These processes are the examples of the model radical reactions of various nature: alkanes chlorination occurs as a radical-chain process, while thiol oxidation is a non chain process. The coordinating and redox properties of sulfur- and halogen-containing compounds differ significantly. Nevertheless, both reactions contain redox stages characteristic for metal complex initiation. The above mentioned processes are also of practical significance. The first one is used in petrochemistry [19,20]. The second one is a promising method for disposal of banned carbon tetrachloride (CTC), as it allows the initial organic chlorine to be fully utilized to form valuable commercial products [21,22].

We have previously shown the metal complexes with ILs grafted on silica gel by covalent bonding between hydroxyl groups of the surface and functional groups of the ionic liquid to be more active in the chlorination process than the catalytic systems, obtained by physical adsorption of the IL complex of the mineral support [22].

Compositions based on copper (II) chloride and quaternary ammonium bases either in solutions or adsorbed on a surface were proposed as catalysts for this reaction [21,22]. The main shortcoming of the method is fast catalyst deactivation, which is caused by necessity to perform the process at high temperature. We have stated that this shortcoming can be avoided if transition metal complexes with thermally stable quaternary ammonium bases (QAB) derived from imidazole, pyridine or short-chain alkylamines immobilized on the silica gel surface are used together with aliphatic alcohols (ethanol or propanol). Using this approach, the yield of chloroalkanes was increased and the catalyst stability was

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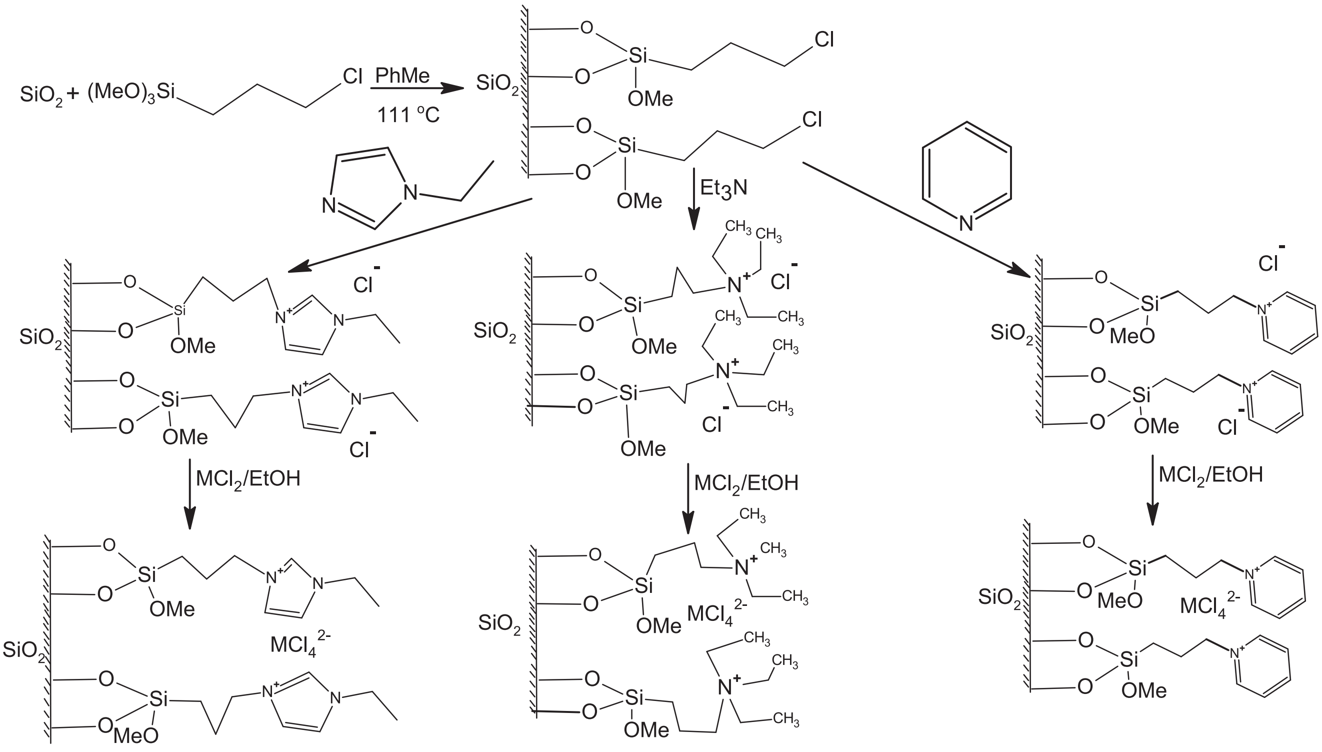

Fig. 1. The scheme of the immobilization of the ionic liquids complexes on the supports.

enhanced, and thus the catalysts became suitable for repeated use without loss of activity.

2. Experimental

2.1. The catalysts synthesis

The following supports were used to obtain the catalysts: silochrome C-120 (surface area ≈120 m^2/g, pore diameter = 40–45 nm), silica gel KSK-2 (surface area ≈300 m^2/g, pore diameter = 12–15 nm), Perlkat (surface area ≈300–450 m^2/g, pore diameter = 9–10 nm).

The Cu(II), Co(II) and Mn(II) chloride complexes with immobilized N-ethyl-N′-propylimidazolium chloride (EtPrImCl–SiO_2) on KSK were prepared by a reported procedure [9]. The difference was that the quaternization was carried out in a vacuum rather than in dry argon.

The grafted catalysts (on KSK, Perlkat and silochrome) with propylpyridinium chloride was prepared by immobilizing the cation (see Fig. 1), using the technique, described in [23] with a slight modification.

Typical synthesis of the catalyst was performed as follows: At the first stage 3-chloropropyltrimethoxysilane was added to dehydrated SiO_2 (silochrome, KSK or Perlkat). Toluene was used as a solvent. Weight ratio of the support and modifier was 2:1. The process was performed in a flask equipped with a Dean and Stark distillation head and a reflux condenser. The reaction mixture was boiled until the water stopped accumulating; then the solid phase was filtered off, washed with dry toluene using 10 ml of solvent per gram of support, and dried on air. On the next step the quaternization was done as follows: 2.8 ml of pyridine reacted with 2.0 g of the modified in a sealed glass ampoule at 160 °C under intense stirring for 6 h. After this the excess of pyridine was washed off with 25 ml of ethanol under intense stirring, and then the solid was filtered off and dried under 50–70 °C. The difference from the technique, described in [23] is as follows. In the literature method on the first stage the modifier of the surface (3-chloropropyltrimethoxysilane) interacted with amine to form quaternary ammonium salt, and then the surface was modified with this salt. The modification with the triethylpropylammonium chloride is described in [22].

To obtain the grafted complexes, ethanolic solution of metal chloride ($CuCl_2$, $MnCl_2$, $CoCl_2$) reacted with the modified SiO_2 in a flask under intense magnetical stirring for 1 h and slight heating (50–70 °C). After that the solid phase was filtered off and dried on air.

2.2. Physico-chemical study of the catalysts

The grafting of the complex was monitored by IR spectroscopy for KBr pellets using an Infralum FT-801 FT IR spectrophotometer. Treatment of silica gel with the modifying agent induced an irreversible decrease in the intensity of the bands for the terminal surface OH groups (3745 cm^{-1}) and appearance of the bands at 2800–3000 cm^{-1}, which did not disappear even after long-term keeping of the samples in a thermostat at 180–200 °C.

The diffuse reflectance electronic spectra were measured on an HR4000CG-UV-NIK Ocean Optics instrument with an integrating sphere in the range of 300–1200 nm.

The thermogravimetric measurements were carried out on a Derivatograph-C instrument in air and under argon at a heating rate of 10 °C/min for ∼15 mg samples.

The amount of metal on the surface was determined by complexometry. The amount of modifier on the support surface was stated by C-, N-, H-elemental analysis on a Vario MAX apparatus.

^{13}C NMR spectra were recorded on a BRUKER AVANCE-II NMR 400 with using of solid-state 4 mm H/X MAS probe. A RAMP cross-polarization pulse sequence with SW-TPPM high-power proton decoupling was used. The contact time–2 ms; recycle delay–2 s. The chemical shift scale was referred relatively to the CH_2 group of solid adamantane. A sample for NMR–MAS investigation contained the catalytic sample and 10-fold excess of dodecane-1-thiol. After complete reduction of copper (which was registered as the discoloration