Polysaccharide-inorganic transition metal composites for partial oxidation of cyclohexane

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Abstract: Polysaccharide-containing iron composites with natural sorbent – the montmorillonite from the Tagansky deposit (MMT) have been synthesized by the adsorption method. The natural polymer - chitosan (Chit) have been chosen as a modifier. The method of preparation of composites eliminates the high-temperature stages of calcination and reduction. The developed composites have been studied by various physicochemical methods (IR-spectroscopy, SEM, photoelectrocolorimetry, BET, element analysis). The obtained data indicate the fixing of the polymer and metal ions on the surface of inorganic sorbent. The synthesized composites showed activity in the partial oxidation of cyclohexane at a temperature of 40°C and atmospheric pressure.
Keywords: Polysaccharides, polymer-inorganic composites, chitosan.

1. Introduction

Recently, the development of new materials based on natural polymers and sorbents is relevant. Polysaccharides do not cause the pollution of the environment and their use is not associated with toxic, fire and hazardous substances, due to their biocompatibility and water solubility. In recent decades, interest in composites based on chitosan has increased [1, 2]. The present paper presents data on the synthesis of chitosan-containing iron composites with natural sorbent for use in catalysis.

2. Experimental (or Theoretical)

Synthesis of iron-containing polysaccharide-inorganic composites is based on the adsorption of polysaccharides onto the surface of inorganic material, with further adsorption of metal ions from aqueous solution onto the polymer-modified composite. Natural polymer - chitosan was chosen as a modifier, the support was montmorillonite from the Tagansky deposit, Kazakhstan (MMT). The active phase was iron ions in a form of potassium ferricyanide. The active phase content was 1%.

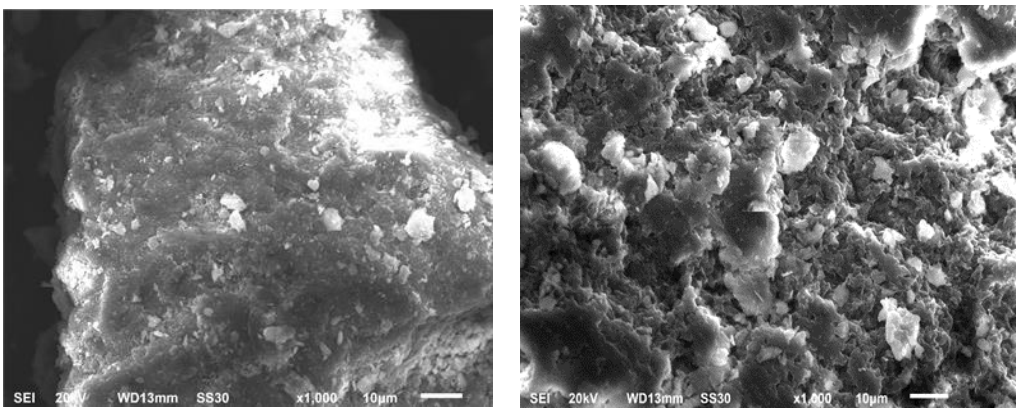
The amount of the metal immobilized on the polymer-modified surface of inorganic material was determined from the change in the concentration of metal ions in the mother liquor before and after sorption by photoelectrocolorimetry (spectrophotometer SF-2000). SEM images of the samples were obtained on an electron microscope JSM-6610 LV ("JEOL" Ltd., Japan) with an accelerating voltage of 15-20 kV. The specific surface area and porosity of the samples were measured using an Accusorb analyzer (Micromeritics, USA). IR spectra were obtained on a Thermo Scientific Nicolet iS5 FTIR spectrometer (USA).

The liquid-phase cyclohexane oxidation by hydrohen peroxide was carried out at a temperature of 313 K and atmospheric pressure. The analysis was performed on chromatograph "Chromos GCh-1000".

3. Results and discussion

The study of texture characteristics and morphology of polysaccharide-inorganic composites was carried out using BET and scanning electron microscopy (SEM) methods

The study of the MMT morphology by SEM microscopy showed that an anisometric form is characteristic for mineral sorbent (Figure 1, a). The surface of the metal-polymer composite is more homogeneous, and consists of superimposed sheets and micro-aggregates of MMT coated with a layer of polymer (Figure 1, b).



a) b)

Figure 1. SEM images of MMT (a) and Fe-Chit/MMT (b)

The measurement of the specific surface area of aluminosilicate and its polysaccharide-modified composites by the method of low-temperature nitrogen adsorption at 77K confirmed the assumption of fixation of chitosan macromolecules on the sorbent surface. The initial specific surface area of MMT (100.7 m^2/g) was reduced by 4.6% and was 96.1 m^2/g when ~ 2% of the polymer was added to the sorbent. A further increase in polymer loading increased the share of blocked MMT surface. Synthesis of the supported polymer-metal complex was carried out by adsorption of iron ions on polysaccharide-modified aluminosilicate. The amount of adsorbed metal was determined by the photoelectrocolorimetry method by the change in the concentration of metal in mother liquor before and after sorption. According to the obtained data, 95% of the introduced metal is adsorbed on the chitosan-modified system which was 1% of the total mass of composite. Interaction of chitosan with potassium ferrocyanide and MMT is confirmed by shifting of the frequency of deformation vibrations of -NH-groups from 1616 cm^{-1} in the IR spectra of MMT-Chit and Chit-$Fe(CN)_6]^{4-}$ composited. The elemental analysis data confirmed that iron content in the final three-component composite was 1% wt.

The iron-containing systems obtained by us were tested in the partial oxidation of cyclohexane to mixture of ketone and alcohol (KA-oil) at a temperature of 40°C and atmospheric pressure. It was found that the process proceeds with 100% selectivity for KA-oil at 24% conversion of the substrate.

4. Conclusions

Thus, the conducted studies indicate the formation of iron-containing chitosan-inorganic composites. It has been shown that the fraction of the blocked surface of support increases with increasing polymer loading. The interaction of the three components was confirmed by different methods. The obtained composites are perspective for further use in the oxidation of cyclohexane.

References

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