



ANILINE MULTIPHASE OXIDATION CATALYZED BY KEGGIN-TYPE HETEROPOLYCOMPUNDS

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In the past few years, our research group has been studying the synthesis, characterization and application of new Keggin type heteropolycompounds (HPA) for the oxidation reactions. Recently, we discovered a more convenient procedure for the oxidation using aqueous hydrogen peroxide promoted by HPA in a triphasic system; comprising an aqueous solution of hydrogen peroxide, an organic solvent and an ionic liquid. Addition of Aliquat 336 to such a system, leads to formation of a third phase which resides between the aqueous phase and the organic phase. In this paper we describe the selective oxidation of aniline to nitrosobenzene employing multiphase conditions, several HPA were examined as catalysts at room temperature, while additional control experiments were conducted using homogeneous conditions (acetonitrile), biphasic conditions (isooctane and H₂O). Additionally, the effect on selectivity by reaction temperature variation was investigated, using these catalysts: H₃PMo₁₂O₄₀, H₆PBMo₁₁O₄₀, H₆PAIMo₁₁O₄₀, H₄PVMo₁₁O₄₀, H₆PAI_{0.5}V_{0.5}Mo₁₁O₄₀, H₇PV₂Mo₁₀O₄₀, H₉PV₆Mo₆O₄₀, H₁₁PV₈Mo₄O₄₀ and H₅PBiMo₁₁O₄₀, respectively.

V into primary structure of HPA improved catalytic activity, which was attributed to an increase in the reduction potential. This potential directly correlates with V-number present into primary structure. The more remarkable effect on conversion was Al incorporation in replace of Mo atoms. One atom of Al increased to conversion from 36 % to 74 %. As partial conclusion, the most active catalyst under the examined conditions contained both Al and V on the Keggin primary structure.



$\text{H}_6\text{Mo}_{11}\text{PA}_{10.5}\text{V}_{0.5}\text{O}_{40}$ catalyst gave 90 % conversion with 100 % selectivity towards nitrosobenzene formation. Further experiments were carried out to examine the influence of iron, by substitution of proton on HPA structure. The multiphasic reaction system (d) was employed using the following HPA: two catalysts containing Fe ($\text{HFePVMo}_{11}\text{O}_{40}$ and $\text{H}_{0.5}\text{FePV}_{0.5}\text{Mo}_{11}\text{O}_{40}$) and two catalysts without Fe for comparison ($\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ and $\text{H}_{3.5}\text{PV}_{0.5}\text{Mo}_{11}\text{O}_{40}$). Furthermore, the Fe substituted catalysts promoted higher conversions within shorter time frames also compared with previous catalysts. Such improved activity cannot be ascribed to the variation of reduction potentials, since the presence of Fe does not affect this value; it is more likely to be due to the increased of HPA strength acidity. The Fe-HPA is indicated higher electrode ionization potentials, it is important said that Fe atom are on secondary structure of Keggin HPA. Once the reaction conditions for the selective oxidation of aniline to nitroso and to nitro had been optimized, the reaction was extended to other substrates. In all cases the conversion to the related nitroso compound was completed in a short reaction time and the products were obtained in excellent yields (85-99%), and high selectivity. In addition, it reports the results for the selective oxidation of different anilines to nitro compounds. The reaction was performed at 60 °C and, also in this case, yields were very high (99-100%), and the reaction was extremely selective.

In this work it was demonstrated that the multiphasic system gives better results in the oxidation of aniline to nitrosobenzene using hydrogen peroxide as oxidant in presence of Keggin HPA catalysts. It is important emphasize that the use of HPA as catalyst in multiphase system is realized in mild conditions: room temperature, atmospheric pressure with low reaction time. In same cases, for conversion 90% at 2 h was obtained. On the other hand, the synthesis of HPA is simple and cheap in comparison other catalytic system used for this reaction.