Valorization of essential oils by CoO-catalyzed allylic oxidation of monoterpenes

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Terpenic compounds are important biomass-based renewable feedstock that can be used to replace the present petroleum-based source of hydrocarbons. In particular, these compounds represent a sustainable supply of intermediates for the fine chemical industry, e.g., the manufacture of flavors and fragrances. There is much interest in the catalytic transformations of these natural products to more valuable chemicals, in particular, via aerobic oxidations over cobalt and palladium catalysts. We report herein the cobalt oxide-catalyzed oxidation of various monoterpenic alcohols with molecular oxygen aiming to add value to natural ingredients of essential oils. In order to improve catalyst separation, a core-shell silica-coated magnetic support was used for the immobilization of cobalt oxide, CoO. The material was found to be an efficient heterogeneous catalyst for the allylic oxidation of monoterpenes under mild conditions (1 atm O_2 and 40-60^{o}C) in the absence of any co-catalyst, solvent or additives. Limonene and α-pinene were efficiently converted in a variety of oxygenated products with 40-60% selectivity to allylic products. The oxidation of 3-carene resulted in a complex mixture of products without any specific selectivity. On the other hand, β-pineno was almost exclusively converted to the allylic products (94% selectivity). As the reaction occurs in neat substrate and the catalyst can be easily removed magnetically, final mixtures with high concentrations of valuable oxygenated products can be easily obtained. Although several products are formed, for practical purposes their separation is often not necessary as the mixtures themselves show interesting organoleptic properties and can be used directly in fragrance compositions. The higher the concentration of mono-oxygenate products in the essential oil (and lower the concentration of non-functionalized terpene), the more stable is the fragrance and more valuable is the oil obtained.

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