

Allylic oxidation of cyclohexene by O₂ over nano TiO₂-Fe₂O₃ oxides

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Introduction

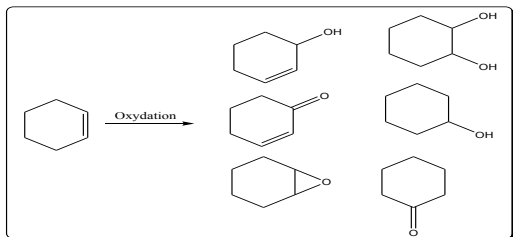
The allylic oxidation of olefins is an important reaction in the fine chemicals industry. Indeed, α , β -unsaturated ketones and alcohols can be produced through these reactions [1,2]. Oxidants such as TBHP or H₂O₂ are frequently used for these reactions in the presence of metal catalysts. These are efficient oxidants. Nevertheless, they have some drawbacks which can be summarized as follows:

- TBHP is an expensive oxidant which does not respect the environment
- H₂O₂ is less hazardous than TBHP, but there is still too expensive.
- TBHP and H₂O₂ often direct reactions to non allylic oxidations, hence low selectivity to α , β unsaturated alcohols and ketones [3].

Oxygen molecular or from air can be a good alternative to these oxidants to achieve oxidation reactions under conditions of green chemistry and with lower costs.

Various catalysts were used for such reactions [4]. Modified or non TiO₂ oxides have shown very interesting catalytic performances in oxidation of olefins with TBHP and H₂O₂. However, attempts with molecular oxygen or air as oxidant and TiO₂ based oxides are very rare.

The aim of this work is to prepare TiO₂-Fe₂O₃ mixed oxides and test their catalytic performances in cyclohexene oxidation (scheme 1).



Scheme1: Main products of cyclohexene oxidation

Materials and Methods

Nano-TiO₂-Fe₂O₃ composites were prepared by a sol gel method, following the protocol described by TK Kundu and col.[5].

A TiO₂ sol was prepared by hydrolysis of a precise amount of tetraisopropylorthotitanate (C₁₂H₂₈O₄Ti) in 40 mL of a mixture of acetic acid and ethanol in a volume ratio of 25: 75. This mixture, designated (a), was stirred for 1 h.

A solution (b) containing a known weight of Fe (NO₃)₃.6H₂O dissolved in 10 mL of distilled water was prepared and then introduced into the mixture (a). The resulting mixture was stirred for 1 h to give the final sol.

This sol was kept stirring at room temperature for 72 h. Finally, the recovered solids were heat-treated in air at 400°C for 4 h.

To examine the influence of relative contents of Ti and Fe we have prepared different materials with different ratios of Ti/Fe

Materials were characterized by elemental analysis, DRUV-vis, FTIR, XRD and BET

Catalytic Test: The oxidation reaction of cyclohexene was performed in a static reactor at a pressure of 6 bar of oxygen and at 80°C.

Results and Discussion:

Characterization: the characterization results confirmed the presence of the anatase phase of TiO₂ and different species of iron oxides on the surface. Ti-Fe-O bonds have also been identified.

Catalytic tests: The results of the catalytic tests are shown in Table 1.

They clearly show that introduction of iron improves the catalytic performances of TiO₂ in terms of activity and selectivity to the cyclohexenone. Indeed, the activities of mixed oxides are greater than TiO₂. Moreover, the selectivities are completely changed when switching from TiO₂ to TiO₂-Fe₂O₃ mixed oxides. At low iron content, this selectivity is 93% of cyclohexenone. This selectivity decreases in favor of the cyclohexenol by increasing iron content, but still very high (above 70%).

Table1. Cyclohexene Oxidation with O₂ over TiO₂-Fe₂O₃ mixed oxides.

m_{cat}=0,1 g, t=24 h, T=80°C, solvent : n-heptane, PO₂=6bar.

Catalyst	C(%)	S _{ENONE} (%)	S _{ENOL} (%)	S _{OL} (%)	S _{ONE} (%)	S _{EPO} (%)
Ti	10,6	-	-	100	-	-
TiFe-S9	28	93	07	-	-	-
TiFe-S4	19	86	14	-	-	-
TiFe-S2	42	72	28	-	-	-

C : conversion, S ; selectivity, ENONE : cyclohex-2-enone, ENOL : cyclohex-2-enol, OL : cyclohexanol, ONE : cyclohexanone et EPO : cyclohexane epoxide.

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