Liquid-phase cyclohexene oxidation over X wt % ZrO$_2$-TiO$_2$ (X =5, 10, 15 and 20 %) anatase xerogel.

D. Lahcene$^a$ and A. Choukchou-Braham$^b$

$^a$Laboratory of Chemistry and Environmental Science, Faculty of Sciences exact, University TAHRI Mohamed of Bechar, BP 417 Road Kenadsa Bechar 08000, Algeria.

$^b$Laboratory of Catalysis and Synthesis in Organic Chemistry, Faculty of Sciences, University A. Belkaid of Tlemcen, B.P. 119 Tlemcen 13000, Algeria.

The ZrO$_2$-TiO$_2$ mixed oxides have been prepared by several techniques, which include sputtering, chemical vapor deposition, pulsed laser deposition and sol–gel process [1, 2]. These mixed oxides are strong solid acids showing catalytic activity in different acid catalyzed reactions, such as isomerization and cracking alkanes, hydration and polymerization of alkenes [3]. Upon oxidation of cyclohexene, which has activated hydrogen at allylic position, it undergoes annoying olefinic oxidation at the double bond in addition to allylic oxidation. It is believed that due to an attack of oxidant at the allylic position as well as at the double bond simultaneously, it lead to the formation two allylic products (2-cyclohexen-1-ol, 2-cyclohexen-1-one) and two epoxidation products such as cyclohexene epoxide, and cyclohexane-1,2-diol [4, 5]. In this work, we report the sol–gel synthesis of X wt % ZrO$_2$–TiO$_2$ (X= 5, 10, 15 et 20%) mixed oxides, calcined at 500°C under air. The prepared catalysts are characterized by physico-chemical techniques like infrared spectroscopy (IR), X-rays diffraction (XRD), Analyses ICP-OES, thermal analysis (ATG-ATD) and specific surface determination (BET) to understand their behavior, and their use as solid catalysts for oxidation of cyclohexene using Tert-butyl hydroperoxide (TBHP) as oxidizer.

X wt % ZrO$_2$–TiO$_2$ mixed oxides presents a crystalline structure with the presence of TiO$_2$ anatase phase with a BET surface area between 81-104 m$^2$ g$^{-1}$ their IR-spectra show the Lewis acid sites. This system are strong solids acids showing catalytic activity in different acid catalyzed reactions The best catalytic performance was observed at 6 h reaction time with 15 wt.-% ZrO$_2$–TiO$_2$ catalyst in heptane as solvent at 70 °C. The conversion of cyclohexene was 33 % while the selectivity to cyclohexenol was higher (87 %). The catalyst with different percentages showed good activity on cyclohexene oxidation and selectivity to the allylic oxidation product (Scheme. 1).

\[ \begin{align*}
\text{ZrO}_2\text{-TiO}_2 & \xrightarrow{\text{TBHP 5.5 mol.L$^{-1}$ in decane}} \text{80 °C, 0.1 g , 6 h}} \\
& \text{2-cyclohexen-1-ol, 2-cyclohexen-1-one, cyclohexene epoxide, cyclohexane-1,2-diol} \\
\end{align*} \]

Scheme. 1 : Allylic oxidation of cyclohexene

References


Corresponding author email: drissino@yahoo.fr