



Effect of chemical composition of $\text{Sr}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 1.0$) catalyst and alkali towards efficient and selective epoxidation of styrene



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ABSTRACT

Spinel type strontium substituted calcium (SSC) ferrite $\text{Sr}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 1.0$) catalyst synthesized by citrate-gel combustion method are well characterized by various techniques such as TG-DTG, FT-IR, X-ray diffraction, SEM, EDS and BET. The crystallization temperature of the spinel particle prepared by citrate gel is 600°C , which is lower in comparison to ferrite prepared by other methods. Among this series of catalysts, $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{Fe}_2\text{O}_4$ which has highest surface area shows the best catalytic efficiency. GCMS analysis revealed that, during the course of reaction the insertion of oxygen takes place selectively than the oxidative cleavage of $\text{C}=\text{C}$ bonds; to give epoxide as major product, while addition of NaOH suppresses further isomerization of the styrene epoxide, thereby increasing the selectivity remarkably to give epoxide as major product. The catalyst containing both Sr^{2+} and Ca^{2+} ions are more active than pure SrFe_2O_4 and CaFe_2O_4 . The synergistic effect of Sr^{2+} , Ca^{2+} ions and greater site preference energy of Sr^{2+} than Fe^{3+} favour the selective epoxidation of styrene in presence of 30% H_2O_2 as oxidant. The optimization and the effect of various reaction conditions on the conversion of styrene and product distribution were also studied.

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1. Introduction

Mixed metallic oxides are designated as an important class of compounds and among them ferrites are the most prominent by virtue of their high electrical resistivity, thermodynamic stability, electro-catalytic activity and resistance to corrosion. Ferrites are better magnetic materials than pure metals because of their high resistivity, lower cost, easy manufacture and superior magnetization properties. Alkaline earth metal ferrites have attracted considerable attention owing to their potential application in high capacity batteries [1], wastewater cleaning [2], low magnetization ferro fluids [3] and as oxidizing agents [4–6].

Spinel ferrites are of great fundamental and technological importance due to their structural, electronic, magnetic and catalytic properties [7–10]. The physico-chemical properties of the ferrites are strongly dependent on the sites and the nature of the catalyst [11,12], which are closely related to the method of

preparation. Epoxidation of styrene is a commercially important reaction for the production of styrene oxide, an important organic intermediate, as versatile and useful chiral building blocks in organic synthesis [13]. Earlier studies reported for the epoxidation of styrene were based on the use of titanium silicate-1 (TS-1) [14–17], Ti-SiO₂ [14,18,19], Ti loaded Mobil Composition of Matter No. 41 (Ti-MCM-41) [17], and titanium and B co-substituted silicate-2 (TBS-2) and TS-1 [20] catalysts, using different oxidizing agents, such as tertiary butyl hydrogen peroxide (TBHP) [18], aqueous H_2O_2 [14,15,19,20], and urea- H_2O_2 adduct [16]. For all the above catalysts, the use of aqueous H_2O_2 resulted in a very poor selectivity for styrene oxide. High-styrene oxide selectivity ($\geq 80\%$) could be obtained using urea- H_2O_2 adduct [16] and TBHP [18] as the oxidizing agents but only at a low-styrene conversion (18% and 10%, respectively). It is, therefore, of great practical interest to find such a catalyst which is much better for the epoxidation of styrene. Recently, Mandelli et al. [21] have observed good catalytic activity and selectivity for γ -alumina in the epoxidation of limonene, cyclohexene and 1-octene by using anhydrous H_2O_2 . However, they observed catalyst deactivation after a certain reaction period (5 h), due to accumulation of the reaction water. Olefin epoxidation is a key transformation in organic synthesis both on a laboratory and on industrial scale, due to the interest in epoxides for the production

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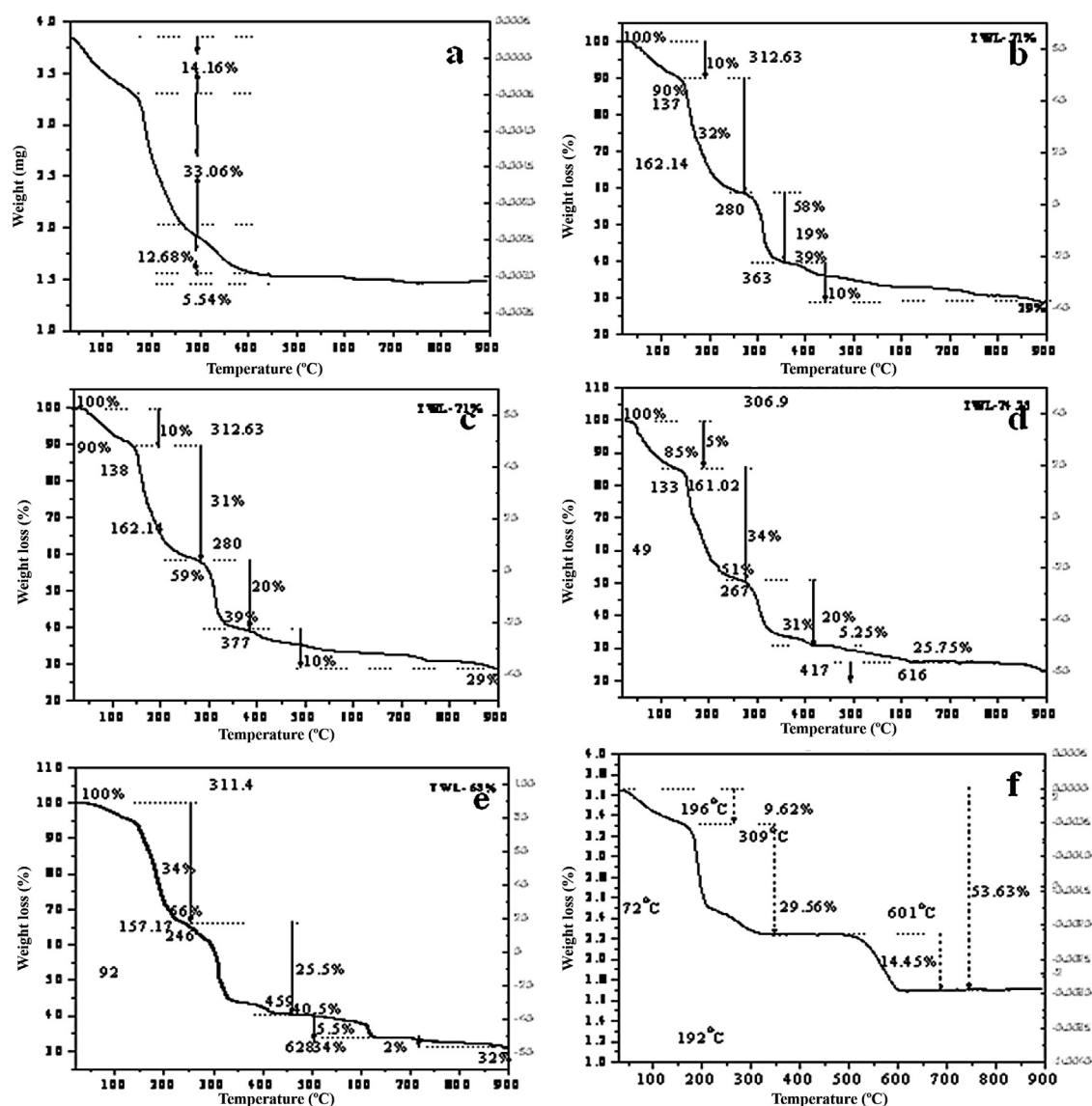


Fig. 1. TG curves of precursors of CaFe_2O_4 (a), $\text{Sr}_{0.2}\text{Ca}_{0.8}\text{Fe}_2\text{O}_4$ (b), $\text{Sr}_{0.4}\text{Ca}_{0.6}\text{Fe}_2\text{O}_4$ (c), $\text{Sr}_{0.6}\text{Ca}_{0.4}\text{Fe}_2\text{O}_4$ (d), $\text{Sr}_{0.8}\text{Ca}_{0.2}\text{Fe}_2\text{O}_4$ (e) and SrFe_2O_4 (f) prepared by citrate gel combustion method.

of chemicals and fine chemicals [22]. The use of hydrogen peroxide for selective epoxidation is highly desirable because it is cheap, the active oxygen content is high, and it is clean, since the only by-product formed is water [23]. Many catalytic systems based on different metals have been reported for the epoxidation of a wide range of alkenes using hydrogen peroxide [24–26].

The alkaline earth metal ferrites like CaFe_2O_4 and SrFe_2O_4 were also used in selective oxidation of styrene but the selectivity of epoxide was very less while benzaldehyde was the major product in acetone and water as the reaction solvent, respectively [5,6]. The present work is undertaken to explore the possibility of combining the advantages of using hydrogen peroxide, a heterogeneous catalyst strontium substituted calcium (SSC) ferrite and solvents from renewable sources (acetonitrile and methanol), with tailored properties, to extend the range of applicability of these catalytic systems to the epoxidation of a more challenging substrate styrene. We report for the first time, the use of a simple, inexpensive and reusable mixed metal oxide, SSC ferrite, $\text{Sr}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0), for the selective epoxidation of styrene in presence of 30% H_2O_2 and NaOH solution in suitable solvent system with very good selectivity and yield of styrene epoxide.

2. Experimental

2.1. Synthesis of catalyst by citrate gel combustion method

Analytical grade calcium nitrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], strontium nitrate [$\text{Sr}(\text{NO}_3)_2$], iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] and citric acid [$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$] (Specialized Pvt. Ltd., Mumbai, India) were used to prepare the strontium substituted calcium ferrites with different compositions $\text{Sr}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$, where $0.0 \leq x \leq 1.0$. The specified volume of metal nitrate solutions was also slowly added to citric acid solution to form the sol. The molar ratio of metal nitrates to citric acid was 1:1. During this procedure, the sol was continuously stirred by a magnetic agitator. Then, the sol was poured in to a dish and heated at 80°C on a hot plate and stirred continuously to transform into a zero gel. At appropriate temperature ignition started and the dried gel burnt in a self-propagating combustion manner until all the gel was burnt out completely to form a fluffy loose powder. The entire combustion process was done in a few minutes. Finally, the as-burnt powders were calcined in the muffle furnace from 600 to 800°C for 2 h with a heating rate of $10^\circ\text{C}/\text{min}$ to obtain the single phase ferrite [5,7].

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