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Original Research Paper

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OXIDATIVE DEHYDROGENATION OF ETHYL BENZENE OVER CERIA MODIFIED COBALT MANGANESE FERROSPINELS

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ABSTRACT Oxidative dehydrogenation (ODH) offers a promising route for styrene (ST) production as an alternative to the conventional direct dehydrogenation process. Nevertheless, the ODH process using O_2 exhibits limited ethylbenzene conversion. Herein, the ODH process with O2 atmosphere using ceria modified cobalt manganese ferrospinels for the efficient conversion of ethylbenzene to styrene is proposed. A series of cobalt manganese ferrospinels (CMF) has been synthesized by the controlled low temperature hydroxide coprecipitation technique and their ceria modification (CMF-Ce) was done by the wet impregnation method. Both CMF and CMF-Ce catalysts were characterized by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), BET surface area, pore size, pore volume measurements, temperature programmed desorption of ammonia (TPD of NH3) and dehydration activity studies using decomposition of cyclohexanol. The catalytic performance of the prepared systems was evaluated through the oxidative dehydrogenation of ethylbenzene. It is observed that the ceria modified catalysts performed better selectivity towards the conversion of ethyl benzene to styrene.

KEYWORDS : Styrene, Ethyl Benzene, Oxidative Dehydrogenation, Ferrospinels

INTRODUCTION

Styrene is primarily used as a precursor to polystyrene, a widely used plastic material. It is a key monomer in the production of copolymers such as ABS (acrylonitrile butadiene styrene), SBR (styrene-butadiene rubber), and SAN (styrene-acrylonitrile), which are vital in automotive, construction, and electronics industries. Currently, catalytic dehydrogenation of ethylbenzene is responsible for nearly 90% of global styrene production; however, it faces significant drawbacks such as a high steam-to-ethylbenzene feed ratio, thermodynamically limited conversion, and complex product separation, all of which contribute to substantial heat consumption [1, 2]. Although the commercial dehydrogenation process is highly energy-intensive due to significant steam consumption, it still requires two reactors in series with interstage heating to reach just 64% ethylbenzene conversion [3, 4]. Hence, it is imperative to develop a new process that enhances styrene production efficiency and addresses the existing challenges of the catalytic dehydrogenation method.

The present study focusses on the activity and selectivity of $Co_xMn_{(1-x)}Fe_2O_4$ (x = 0, 0.2, 0.8 and 1.0) type ferrospinel systems and their ceria modifications in the oxidative dehydrogenation of ethyl benzene. The ceria modified cobalt manganese ferrospinels exhibited remarkable activity and selectivity for the styrene production.

MATERIALS AND METHODS

Catalyst Synthesis

A series of cobalt–manganese ferrospinels, namely $MnFe_2O_4$ (MF), $Co_{0.2}Mn_{0.8}Fe_2O_4$ (MCF-0.2), $Co_{0.4}Mn_{0.6}Fe_2O_4$ (MCF-0.4), $Co_{0.6}Mn_{0.4}Fe_2O_4$ (MCF-0.6), $Co_{0.8}Mn_{0.2}Fe_2O_4$ (MCF-0.8), and $CoFe_2O_4$ (CF), were synthesized via a low-temperature hydroxide co-precipitation method. Their ceria-modified counterparts were subsequently prepared using the wet impregnation technique.

Catalyst Characterization

X-ray diffractograms of the powdered samples were recorded using a Rigaku D/MAX-C instrument with Cu Kα radiation. Thermal stability was evaluated by thermogravimetric (TG) analysis at a heating rate of 10 °C min^{-1}. The stoichiometry of the prepared systems was verified using energy-dispersive X-ray (EDX) spectroscopy. The BET surface area was determined by nitrogen adsorption at liquid nitrogen temperature using a SMART SORB 92/93 analyzer.

The acidity strength and distribution of the samples were determined by temperature-programmed desorption (TPD) of ammonia. The acid strength distribution was then evaluated over the temperature range of 100–600 °C under a nitrogen flow in a stepwise manner. Based on the desorption temperature ranges (100–200 °C, 201–400 °C, and 401–600 °C), the acid sites were classified as weak, medium, and strong, respectively.

Catalytic Activity

Oxidative Dehydrogenation of Ethylbenzene

The reactions were performed in a vapour-phase down-flow silica reactor kept in a cylindrical double walled furnace mounted vertically. 0.5 g of the catalysts activated at 500°C for 2 h was placed in the middle of the reactor. A 20 ml of air/minute along with ethylbenzene was passed through the reactor in the temperature range 400-550°C. The products were analyzed by gas chromatography (Chemito GC 8610).

RESULTS AND DISCUSSION

XRD analysis confirmed the formation of a single-phase spinel structure with good crystallinity in the catalyst samples (Fig. 1). In the cobalt–manganese ferrospinels investigated, compositional variations arise from different Co and Mn ratios in $MnFe_2O_4$; however, due to their similar atomic numbers, the resulting XRD patterns are highly comparable (Figure 1).

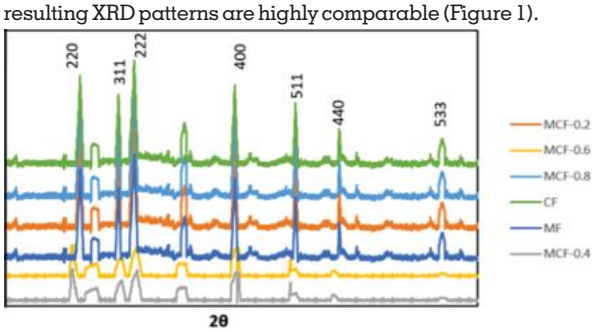

Figure 1: XRD Patterns of Cobalt-manganese Ferrospinels, $Co_xMn_{(1-x)}Fe_2O_4$(x = 0, 0.2, 0.8 and 1.0)

For the ceria-loaded systems, no distinct diffraction peaks corresponding to pure CeO_2 were observed up to 5 wt% loading, indicating a high dispersion of ceria over the ferrite matrix.

The stoichiometry of both the ferrospinel samples and their ceria-modified counterparts shows good agreement with theoretical values, as confirmed by EDX analysis (Table 1).

Table 1: EDX Analysis Data of Cobalt-manganese Ferrospinels and their 5 wt% Ceria Loaded Counterparts.

Catalyst Composition	Weight percentage of				
	Mn	Co	Fe	O	Ce

MnFe2O4	23.82	----	48.43	27.75	----
Co0.2Mn0.8Fe2O4	19.00	5.08	48.26	27.62	----
Co0.4Mn0.6Fe2O4	14.20	10.14	48.08	27.55	----
Co0.6Mn0.4Fe2O4	9.45	15.15	47.93	27.46	----
Co0.8Mn0.2Fe2O4	4.70	20.16	47.76	27.37	----
CoFe2O4	----	25.12	47.60	27.27	----
5Ce-MnFe2O4	23.31	----	44.37	27.39	4.93
5Ce-Co0.2Mn0.8Fe2O4	18.52	4.98	44.18	27.53	4.85
5Ce-Co0.4Mn0.6Fe2O4	13.99	9.95	43.74	27.48	4.84
5Ce-Co0.6Mn0.4Fe2O4	9.25	14.96	43.63	27.36	4.80
5Ce-Co0.8Mn0.2Fe2O4	4.63	19.86	43.57	27.13	4.81
5Ce-CoFe2O4	----	24.83	43.34	26.95	4.88

The ferrite samples synthesized via the low-temperature co-precipitation method exhibit high surface area (Table 2). Upon ceria modification, a decrease in surface area and pore volume is observed, which can be attributed to the partial blockage of micropores by ceria species.

Table 2: BET Surface Area and Pore Volume Analysis Data of Cobalt-manganese Ferrospinels, and their 5 wt% Ceria Loaded Counterparts.

Catalyst Composition	BET Surface area (m2/g)	Pore Volume (cm3/g)
MnFe2O4	153.3	0.5023
Co0.2Mn0.8Fe2O4	112.95	0.3875
Co0.4Mn0.6Fe2O4	105.28	0.3836
Co0.6Mn0.4Fe2O4	97.23	0.3789
Co0.8Mn0.2Fe2O4	85.78	0.3719
CoFe2O4	75.63	0.3614
5Ce-MnFe2O4	136.06	0.2712
5Ce-Co0.2Mn0.8Fe2O4	103.28	0.2701
5Ce-Co0.4Mn0.6Fe2O4	95.68	0.2632
5Ce-Co0.6Mn0.4Fe2O4	85.76	0.2491
5Ce-Co0.8Mn0.2Fe2O4	76.80	0.2253
5Ce-CoFe2O4	63.51	0.2195

Thermogravimetric (TG) analysis reveals that all ferrite systems are thermally stable within the temperature range of 150–800 °C (Figure 2). A sharp weight loss near 100 °C is associated with the desorption of physisorbed water, while a minor weight loss in the 350–400 °C range is attributed to the decomposition of residual nitrate species originating from the precursor solutions.

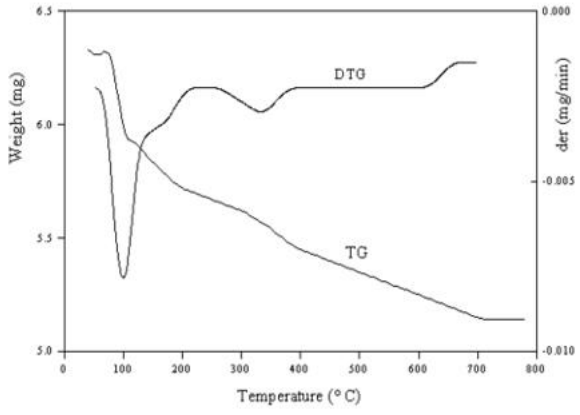

Figure 2: TG-DTG Curves of $Co_{0.4}Mn_{0.6}Fe_2O_4$

The study of surface acidity in catalyst systems is essential, as it plays a decisive role in governing catalytic activity and selectivity. The quantities of ammonia desorbed in the weak (100–200 °C), medium (201–400 °C), and strong (401–600 °C) acid regions are summarized in Table 3. It is observed that incorporation of Co^{2+} ions into $MnFe_2O_4$ reduces the number of strong acid sites but increases the total acidity. Furthermore, ceria modification of cobalt–manganese ferrospinels leads to an increase in both strong acidity and total acidity of the systems.

Table 3: The Acid Site Distribution for Cobalt-manganese Ferrospinels, and their 5 wt% Ceria Loaded Counterparts.

Catalyst Composition	NH3 Desorbed (10-3mmolm-2)			
	Weak (100-200°C)	Medium (201-400°C)	Strong (401-600°C)	Total
MnFe2O4	3.85	4.27	8.38	16.50
Co0.2Mn0.8Fe2O4	3.86	4.70	8.02	16.58
Co0.4Mn0.6Fe2O4	3.88	4.86	7.94	16.68
Co0.6Mn0.4Fe2O4	3.90	4.95	7.89	16.74
Co0.8Mn0.2Fe2O4	3.93	5.09	7.84	16.86
CoFe2O4	3.95	5.10	7.78	16.83
5Ce-MnFe2O4	3.93	5.09	8.38	17.37
5Ce-Co0.2Mn0.8Fe2O4	3.88	5.06	8.57	17.51
5Ce-Co0.4Mn0.6Fe2O4	3.85	5.03	8.71	17.59
5Ce-Co0.6Mn0.4Fe2O4	3.84	5.01	8.92	17.77
5Ce-Co0.8Mn0.2Fe2O4	3.80	4.98	9.13	17.91
5Ce-CoFe2O4	3.80	4.93	9.10	17.83

Catalytic Activity Studies

In oxidative dehydrogenation, the formation of carbon oxides is often a side reaction. The process economy rapidly deteriorates when ethylbenzene is extensively oxidized to carbon oxides. Therefore, the catalyst should be very selective in the minimum production of carbon oxides.

Table 4 presents the comparison of the results of oxidative dehydrogenation of ethyl benzene over Co-Mn ferrites systems. Incorporating cobalt into manganese ferrospinel systems enhances the conversion of ethylbenzene and improves styrene productivity.

Table 4: Product Distribution (wt%) and Selectivity for ODH of Ethylbenzene over Cobalt-manganese Ferrospinels.

Product distribution	Reaction temperature- 350°C, Flow rate- 6mL h-1, air flow rate-20 ml/minute, TOS -2h					
	MF (x=0)	MCF-0.2 (x=0.2)	MCF-0.4 (x=0.4)	MCF-0.6 (x=0.6)	MCF-0.8 (x=0.8)	CF (x=1.0)
Benzene	1.23	1.37	1.36	1.20	0.95	1.31
Toluene	1.02	0.70	0.56	0.48	0.30	0.33
Unreacted EB	43.27	41.73	40.05	37.91	35.58	36.83
C-oxides	2.96	2.97	2.91	2.89	2.95	2.90
Styrene	51.52	53.23	55.12	57.52	60.22	58.63
EB conversion	56.73	58.27	59.95	62.09	64.42	63.17
Selectivity (%)						
Benzene	2.19	2.35	2.26	1.93	1.47	2.07
Toluene	1.79	1.20	0.93	0.77	0.47	0.52
C-oxides	5.21	5.09	4.85	4.65	4.58	4.59
Styrene	90.81	91.35	91.94	92.64	93.48	92.81

Table 5 compares the outcomes of oxidative dehydrogenation of ethylbenzene over Co–Mn ferrite systems loaded with 5 wt% ceria. The ceria modified cobalt manganese ferrites further enhanced both ethylbenzene conversion and styrene selectivity.

Table 5: Product Distribution (wt%) and Selectivity for ODH of Ethylbenzene Over 5 wt% Ceria Loaded Cobalt-manganese Ferrospinels.

Product distribution	Reaction temperature- 350°C, flow rate- 6mL h-1 and air flow rate-20 ml/minute, TOS-2h

	Ce-MF	Ce-MCF-0.2	Ce-MCF-0.4	Ce-MCF-0.6	Ce-MCF-0.8	Ce-CF
Benzene	1.03	1.07	1.06	1.02	0.85	1.05
Toluene	0.98	0.60	0.46	0.37	0.22	0.28
Unreacted EB	33.27	31.86	30.25	26.36	25.48	26.83
C-oxides	1.36	1.27	1.21	1.19	0.98	1.06
Styrene	63.36	65.20	67.02	71.06	72.47	70.78
EB conversion	66.73	68.14	69.75	73.64	74.52	73.17
Selectivity						
Benzene	1.54	1.57	1.52	1.38	1.14	1.43
Toluene	1.46	0.88	0.66	0.50	0.29	0.38
C-oxides	2.03	1.86	1.73	1.61	1.31	1.44
Styrene	94.94	95.68	96.08	96.49	97.24	96.73

The catalytic activity was correlated to the acid properties of the samples (Table 6).

Table 6: Surface Acidity, Ethylbenzene (EB) Conversion and Styrene Yield (%) of the Prepared Ferrospinel Systems and their Ceria Modifications

Catalyst Composition	Total Acidity (10-4 mmol m-2)	EB conversion (%)	Styrene Selectivity (%)
MnFe2O4	16.50	56.73	90.81
Co0.2Mn0.8Fe2O4	16.58	58.27	91.85
Co0.4Mn0.6Fe2O4	16.68	59.95	91.94
Co0.6Mn0.4Fe2O4	16.74	62.09	92.64
Co0.8Mn0.2Fe2O4	16.86	64.42	93.48
CoFe2O4	16.83	63.17	92.81
5Ce-MnFe2O4	17.37	66.73	94.94
5Ce-Co0.2Mn0.8Fe2O4	17.51	68.14	95.68
5Ce-Co0.4Mn0.6Fe2O4	17.59	69.75	96.08
5Ce-Co0.6Mn0.4Fe2O4	17.77	73.64	96.49
5Ce-Co0.8Mn0.2Fe2O4	17.91	74.52	97.24
5Ce-CoFe2O4	17.83	73.17	96.73

The substitution of Mn by Co in the octahedral sites of manganese ferrospinel enhanced the total acidity which improved both ethylbenzene conversion and styrene selectivity. Ceria modification of cobalt–manganese ferrospinels further increased the total acidity of the systems, leading to improved ethylbenzene conversion and enhanced styrene selectivity. Thus, Co-Mn series and their ceria counterparts were found to be good catalysts for oxidative dehydrogenation of ethylbenzene.

CONCLUSIONS

Various compositiions of cobalt manganese ferrospinels with general formula $Co_xMn_{(1-x)}Fe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) and their ceria modifications can be effectively used for the oxidative dehydrogenation of ethylbenzene to styrene. The acid properties of the catalysts vary with the successive incorporation of cobalt ions into the manganese ferrospinel and with their ceria modifications. All the catalysts samples especially ceria modified systems exhibited high activity and remarkable selectivity for styrene. A moderate amount of acid sites are mandatory for the appreciable ethylbenzene conversion and styrene selectivity.

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