

Enhanced activity for oxidative dehydrogenation of ethylbenzene to styrene using cobalt substituted copper chromite spinels

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Cobalt substituted copper chromite spinels ($\text{Cu}_{1-x}\text{Co}_x\text{Cr}_2\text{O}_4$, where $x = 0, 0.25, 0.5, 0.75$ and 1.0) have been prepared by homogeneous co-precipitation method. The materials have been characterized in detail by X-ray diffraction, BET surface area, Scanning Electron Microscopy, Energy Dispersive X-ray analysis and FT-IR spectroscopy. Powder X-ray diffraction pattern reveals the spinel phase formation and energy dispersive X-ray analysis indicates the correct stoichiometry. Oxidative dehydrogenation of ethylbenzene to styrene is conducted with air as an oxidant. It is shown that the catalysts are highly active. Reusability studies of the catalysts show that cobalt substituted copper chromite spinels are stable under the reaction conditions.

Keywords: Spinel, Ethylbenzene, Styrene

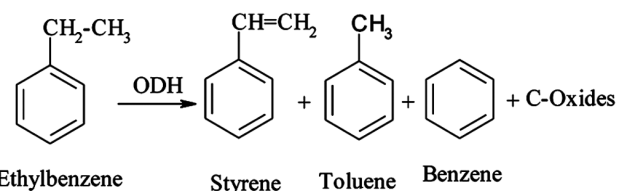
The catalytic dehydrogenation of ethylbenzene is the main method of styrene production, which is one of the most important basic chemicals as a monomer of synthetic polymers. The process is performed at elevated temperatures ($550\text{-}650^\circ\text{C}$) in the presence of potassium doped hematite catalysts. Additional promoters (e.g. Cr_2O_3 , Ce_2O_3 , MgO and MoO_3) are used in order to enhance the activity and selectivity, as well as stability of the catalytic system. Ethylbenzene dehydrogenation is endothermic and limited by thermodynamic equilibrium. An excess of superheated steam is therefore used to supply the heat of reaction and shift the equilibrium to higher styrene yields by a decrease in the partial pressures of reactants¹⁻⁴. Oxidative dehydrogenation of ethylbenzene was proposed as an alternative route in styrene production^{5,6}. Due to the exothermic effect of oxydehydrogenation, a higher conversion of ethylbenzene at significantly lower temperatures can be obtained compared to that in a classical

Note

dehydrogenation process. The schematic representation of the ethylbenzene dehydrogenation is shown in Scheme 1.

Figueiredo *et al.* investigated in detail the oxidative dehydrogenation of ethylbenzene over activated carbon catalysts and studied the catalytic deactivation⁷. They suggested a redox mechanism of the Mars-van-Krevelen type, where the quinone surface groups are reduced to hydroquinone by the adsorbed ethylbenzene, and re oxidised back to quinone by oxygen. The ODH of ethylbenzene was studied over $\text{Mg}_3(\text{VO}_4)_2\text{-MgO}$ systems by Oganowski *et al.* and their findings showed that magnesium orthovanadate forms with magnesium oxide an active biphasic system very efficient in the ODH of ethylbenzene to styrene.

Spinel oxides were reported to be an active catalyst in the oxidative dehydrogenation of ethylbenzene. Krishnasamy *et al.*⁸ studied the oxidative and non-oxidative dehydrogenation of ethylbenzene over Zn-Fe-Cr ternary spinel systems. They revealed that a redox cycle involving $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ is the active site for this reaction. Mathew *et al.*⁹ prepared ferrites of copper and cobalt and studied the ODH of ethylbenzene. They have the same conclusion as proposed by Krishnasamy and explained the results with the mechanism of dehydrogenation of ethylbenzene proposed by Wang and Krouse. Strong basic sites facilitate the formation of toluene whereas strong acid centres result in high yield of benzene. The active site balanced with acidic and basic sites is important for an efficient ethylbenzene dehydrogenation. On the basis of these reports, in the present investigation, we studied the oxidative dehydrogenation of ethylbenzene with air as an oxidant over cobalt substituted copper chromite spinel catalyst.



Scheme 1 — Reaction scheme of oxidative dehydrogenation of ethylbenzene

Experimental Section

Preparation of catalysts

The catalysts were prepared by co-precipitation method¹⁰⁻¹². A mixture consisting of 10% solutions of copper nitrate, nickel nitrate and chromium nitrate for $\text{Cu}_{1-x}\text{Co}_x\text{Cr}_2\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75$ and 1) series were taken in appropriate mole ratios and the mixture was heated to 343–353 K. To this hot mixture a 15% ammonia solution was added drop wise with constant and uniform maintained at this temperature for 2 h and aged for one day. The precipitate was filtered, washed and dried at 353 K for 24 h and calcined at 923 K for 8 h. The prepared samples were designated as follows (Table 1):

Catalyst characterizations

Powder X-ray diffraction patterns of the catalysts were recorded on a Rigaku D-max C X-ray diffractometer using Ni filtered Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) in the region 10–70°. Elemental analysis of the catalysts was carried out by EDX analysis on a Stereoscan 440 Cambridge, UK, energy dispersive X-ray analyzer used in conjunction with SEM. Surface area of the catalysts was calculated by measuring the adsorption of nitrogen at liquid nitrogen temperature in a conventional BET system. Two to four milligrams of each substance was pressed with 200 mg of KBr. The spectra were recorded in an AVATAR 370 Thermo-Nicolet FT-IR spectrometer in the region 400–4000 cm^{-1} .

Catalytic tests

The oxidative dehydrogenation of ethylbenzene to styrene in the presence of air as oxidant was carried out at 500°C over all the spinel catalysts prepared. The reaction was carried out in the air flow rate of 70 mL/minute for two hours. 0.5 g of catalyst is used for the reaction. The products of the reaction were analyzed by a gas chromatograph (Chemito GC 1000) equipped with a flame ionization detector and a capillary column (SE-30 capillary column with 0.2 mm ID and 30 m length).

Results and Discussions

Surface characterization

The catalyst materials were characterized for evaluating the morphology and structure. The prepared samples were first subjected to powder X-ray diffraction. X-ray diffraction studies indicate that the peaks are sharper and are crystalline in nature.

Table 1 — Catalyst composition designation

1.	CuCr_2O_4	CCr
2.	$\text{Cu}_{0.75}\text{Co}_{0.25}\text{Cr}_2\text{O}_4$	CCoCr-1
3.	$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Cr}_2\text{O}_4$	CCoCr-2
4.	$\text{Cu}_{0.25}\text{Co}_{0.75}\text{Cr}_2\text{O}_4$	CCoCr-3
5.	CoCr_2O_4	CoCr

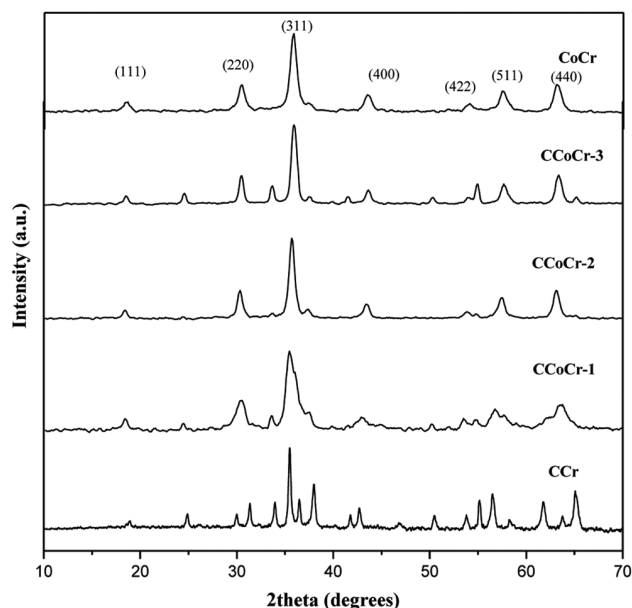


Fig. 1 — XRD profiles of $\text{Cu}_{1-x}\text{Co}_x\text{Cr}_2\text{O}_4$ series spinels.

The theoretical and experimental dhkl values for simple spinels are well coordinated. Interestingly, it was also observed that the mixed chromites gave much identical XRD patterns with those of the simple chromites. Fig. 1 shows the powder XRD patterns of all the materials. The crystallite sizes are calculated from Debye Scherrer formula applied to the major intense peak and are found to be in the range 15–39 nm.

The FTIR spectra of the samples are given in Fig. 2. The two strong absorption bands observed in the spectra of the samples are at 630 and 525 cm^{-1} . The bands at higher and lower wavelength regions are assigned to the vibrations of tetrahedral metal oxygen bond (Cu–O and Ni–O) and octahedral metal–oxygen bond (Cr–O) respectively. The bands at 1640 and 3420 cm^{-1} indicate the presence of surface hydroxyl and coordinated water.

The results of elemental composition by EDX analysis and surface area of this series of catalysts are presented in Table 2. The experimental and theoretical values of Cu, Co and Cr agreed well and indicated correct stoichiometry of the spinel. On

cobalt substitution, surface area increased. A maximum BET surface area of 65.1 m²/g was shown by CoCr catalyst

Scanning electron micrographs were recorded to get the surface morphology of the catalysts. SEM

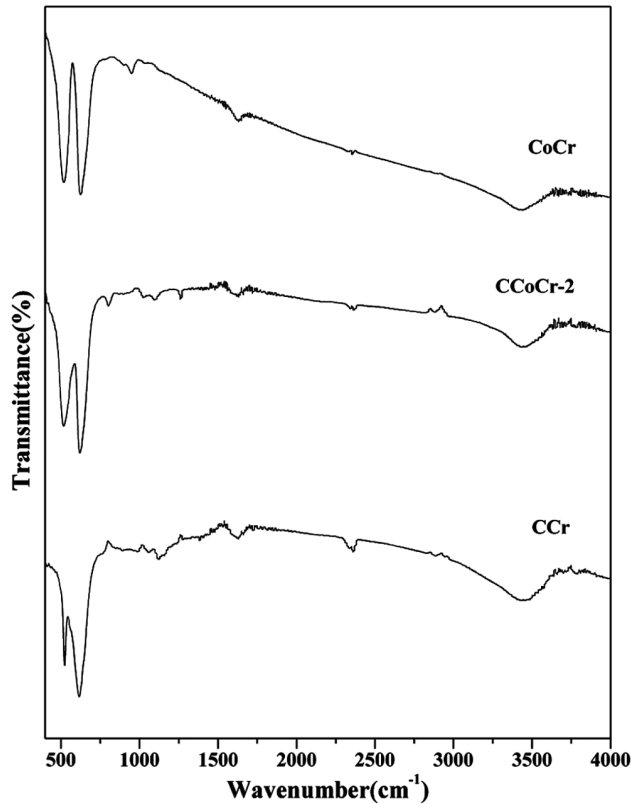


Fig. 2 — FTIR spectra of Cu_{1-x}Co_xCr₂O₄ series spinels

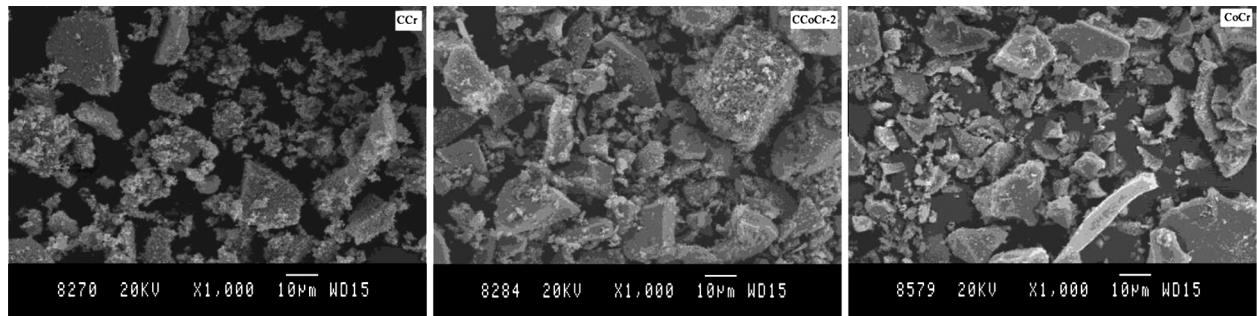


Fig. 3 — SEM Pictures of Cu_{1-x}Co_xCr₂O₄ series spinels

Table 2 — Elemental composition, surface area and crystallite size of the catalysts

Catalyst	Atom Percentage			BET Surface Area(m ² /g)	Pore Volume (cc/g)	Crystalline Size (nm)
	Cu	Cr	Co			
CCr	34.4	65.6	-	6	0.02	39
CCoCr-1	26.4	66.1	7.6	23.0	0.07	16
CCoCr-2	16.0	65.9	18.1	27.3	0.09	16
CCoCr-3	12.2	67.5	20.3	32.5	0.11	16
CoCr	-	67.2	32.8	65.1	0.15	15

pictures of some of the samples are given in Fig. 3. It is clear that samples are aggregates without shape definition.

Catalytic performance

The oxidative dehydrogenation of ethylbenzene to styrene in the presence of air was carried out at 500°C over all the spinel catalysts prepared (Table 3). Moderate ethylbenzene conversion and more than 85% selectivity to styrene was achieved over all the catalytic systems studied. Toluene, benzene and carbon oxides were also formed as side products during this reaction.

Ethyl benzene conversion increased with cobalt substitution and maximum conversion was shown by cobalt chromite catalyst.

A plausible mechanism for the oxidative dehydrogenation of ethylbenzene is described below. At first, ethylbenzene is coordinated to the acid site of the catalyst and the basic group adjacent to the acid site abstracts the α - hydrogen from the co-ordinated ethylbenzene to give a stable adsorbed species. The OH group thus formed over the catalyst surface then abstracts the β - hydrogen and the subsequent desorption of water activates the molecular oxygen. The reversibly adsorbed oxygen is converted to O⁻ species over the catalyst surface, which regenerates the active site.

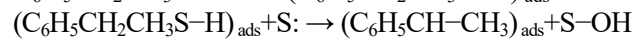
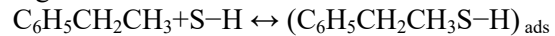
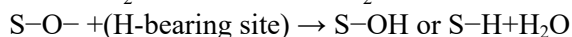
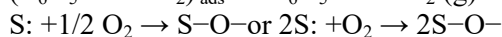
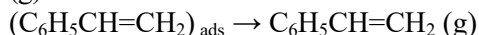
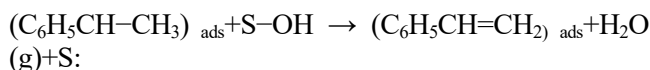


Table 3 — Oxidative dehydrogenation of ethylbenzene over the prepared catalysts

Catalyst	Ethylbenzene conversion (wt %)	Product selectivity (%)			
		Styrene	Benzene	Toluene	C-Oxides
CCr	29.0	88.7	3.2	2.7	5.3
CCoCr-1	37.5	85.6	4.9	4.2	5.2
CCoCr-2	38.7	92.0	3.9	1.7	2.3
CCoCr-3	40.5	90.5	3.9	1.9	5.9
CoCr	43.5	87.3	4.7	2.6	5.4



Regeneration and Stability

To study the stability of the catalysts, recycling experiments with regenerated catalysts were carried out. The procedure adopted was as follows. After 2 h reaction, the catalyst was recovered by hot filtration, washed several times with acetone, dried at 80°C overnight and calcined for 8 h at 650°C. The recovered catalysts were reused for oxidative dehydrogenation of ethylbenzene under the same reaction conditions. The result obtained with regenerated catalysts is presented in Table 4.

Ethyl benzene conversion remained almost constant for the first two cycles and showed a decrease for the third and fourth cycle. There was a small variation in styrene selectivity up to the third cycle, after which it remained nearly constant.

Acknowledgment

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