Magnetically Separable Sustainable Nanostructured Catalysts Pd/ $Mg_{(1-x)}Mn_xCo_2O_4$ used in Heck coupling reaction

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Abstract

Mixed metal oxides have attracted significant attention as catalysts for various organic reactions. In this study, we have synthesis Pd/$Mg_{1-x}Mn_xCo_2O_4$ catalyst for organic transformation. While Mg substituted magnesium cobaltite prepared by sol-gel auto combustion technique. This synthesized material is characterized by different spectroscopic techniques such as XRD, SEM, EDAX and VSM analysis. The XRD studies show the formation of cubic spinel phase with average crystallite size of 33 nm. SEM shows spherical interlinked fibrous morphology. The purity of the material analyzed by EDAX analysis. A room temperature magnetization result shows a ferromagnetic behavior decreases with increase in Mg content. With Palladium is supported on these characterized materials and catalytic performance were studied over Heck coupling reaction it is found that 10% Pd supported $Mg_{0.5}Mn_{0.5}Co_2O_4$ shows ameliorate result.

Key words: - Sol-gel synthesis, XRD, SEM, EDAX.

1. Introduction

During the last decades, there has been an increasing attention inmixed metal oxides because of their remarkable dielectric, magnetic and optical properties, owing to both the broad applications in various technological areas. Number ofdifferent methods have been discovered to prepare mixed metal oxides such as, citrate precursor [1], forced hydrolysis [2],spray pyrolysis [3], co-precipitation[4], hydrothermal [5],ceramic method [6] and sol–gel[7].

The vinylation and arylation of olefin with aryl or vinyl halides was developed independently by Mizorokiand Heck[8-9] about 50 years ago and universally known as Heck reaction. Palladium catalyzed Heck reaction between aryl halide and alkenes is a dignified reaction in modern organic synthetic chemistry [10-12]. The reaction is generally catalyzed by either Pd(II) complexes or Pd(0) [13-14]. In order to entrap the problems, like air sensitivity and catalyst recovery associated with reactions under homogeneous conditions, heterogeneous catalytic systems were developed. In recent years, Heck reaction has been catalyzed by palladium supported on mesoporous Carbon [15],grapheme oxide[16], zeolites[17], palladium/Nb-MCM-41[18],charcoal[19], polyionic resins[20], polymers[21].

In present work, we have prepared Pd /$Mg_{1.x}Mn_xCo_2O_4$ by solution reduction method, while $Mg_{1-x}Mn_xCo_2O_4$ were prepared by using simpleSol-gel auto combustion method and used as a support for preparation of palladium heterogeneous catalyst. This Pd/$Mg_{1.x}Mn_xCo_2O_4$were studied for heck coupling reaction.

2. Experimental details

2.1. Chemicals

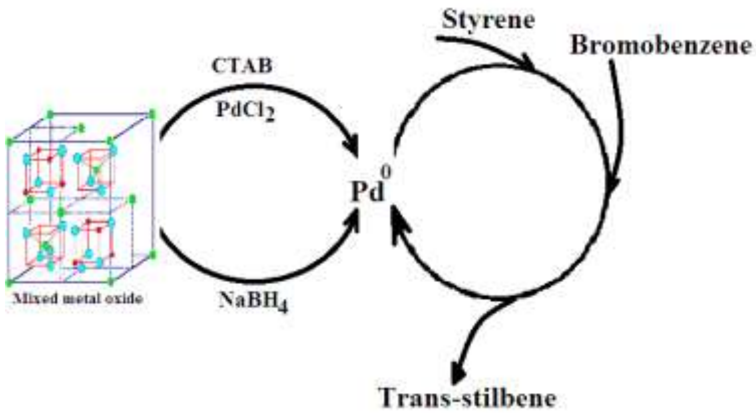
The support $Mg_{1.x}Mn_xCo_2O_4$(x = 0.0, 0.25, 0.50,0.75, 1.0) were synthesized by simple sol–gel auto combustion method. The A. R. Grade cobalt nitrate [$Co(No_3)_36H_2O$], manganese nitrate [$Mn(No_3)_24H_2O$], magnesium nitrate [$Mg(No_3)_26H_2O$],citric acid [$C_6H_8O_72H_2O$] and ammonia solution[NH_4OH] were used as precursor materials and experimental detail were reported in our previous paper[22].While Pd/$Mg_{1.x}Mn_xCo_2O_4$were prepared by solution reduction method. The A.R. grade $PdCl_2$, $NaBH_4$, CTAB and prepared $Mg_{1.x}Mn_xCo_2O_4$were used as precursor for catalyst.

2.2. Preparation of catalyst

The catalyst was prepared as, Sodium borohydride,$Mg_{1-x}Mn_xCo_2O_4$ and 50 ml distilled water was taken in a beaker and stirred for 10 min. In another beaker prepares CTAB solution. These two Solutions were mixed and calculated quantity of $PdCl_2$ solution were added drop wise under constant stirring. The resulting gel was stirred for next 1 hr. for homogenization and solid material were separated by centrifugation technique and solid particles were washed several times with water & acetone till the filtrate was neutral to litmus and dried.

2.3. Reaction procedure

The Heck reaction of styrene with bromobenzene was carried out using these catalysts. A typical reaction was carried out in the air, Styrene 0.68 mL(6 mmol),Bromobenzene 0.42 mL (4 mmol), K_2CO_3 1.646g (12 mmol), Pd/$Mg_{1-x}Mn_xCo_2O_4$ 5wt% (0.074g) with respect to reactants and solvent 5 mL was taken in a round bottom flask connected to water condenser and heated in an oil bath at 100 °C with constant stirring. The reaction was mentored regularly by TLC. After 9 hr, the reaction was completed with 5 mL of water and the catalyst was filtered. Next 50 mL of water was added to the filtrate and the product was extracted with ether. The final product was purified by column chromatography using silica gel (60-120 mesh) with petroleum ether as eluent.



The influence of changing the composition of $Mg_{1-x}Mn_xCo_2O_4$ which was loaded with 2% of Pd has been studied under standardized conditions and the results are given in Table 2.The catalysts with higher yield are remarkably active and selective for the product formation. The higher yield catalyst, i.e. 2%Pd/$Mg_{0.5}Mn_{0.5}Co_2O_4$ was studied to find its effect on Heck cross-coupling reaction at different temperature and results are tabulated in table 3.

Characterization

Trans-stilbenem.p. 124ºC; IR (KBr): 2926, 1597, 1457, 962, 762, 693, 524; 1H NMR (CDCl3): δ 7.28 (t, 2H), δ 7.39 (t, 4H), δ 7.55 (d, 2H), δ 7.15 (s, 2H).

3. Result and Discussion

3.2. XRD studies

The X-ray diffraction pattern of prepared material of the system $Mg_{(1-x)}Mn_xCo_2O_4$(x = 0.0, 0.25, 0.50, 0.75, 1.0) carried out byPhilips PW-1710 X-ray diffractometer with CuKa radiation and sintered at 600° for 5 hr are shown in **Fig.1.**The XRD pattern shows the characteristic peaks at 31.3°, 36.9°, 44.8°, 55.7°, 59.4° and 65.3° according to JCPDS Card No. 23-1237, which can be indexed to (220), (311), (400), (422), (511) and (440) planes of the cubic spinel with Fd3m space group. The sharp peaks observed in the XRD pattern demonstrate a crystalline phase of the samples. Lattice constants, Crystallite size, X–ray density and physical density are shown in **table 1.**

3.2 SEM studies

The SEM images of the $Mg_{(1-x)}Mn_xCo_2O_4$ (0 < X < 1)samples are shown in **Fig.2**(SEM Model JEOL-JSM 6360).Aggregate spherical particle morphology was observed for x=0.0, 0.5 and 1. All the SEM images have similar aggregate shape but their sizes are markedly different. The $MgCo_2O_4$ has smaller particle size as compared to the $MnCo_2O_4$. This is due to the differences in ionic radii of Mg^{2+}(0.65Ǻ) and Mn^{2+} (0.80Ǻ).

3.3 EDAX studies

EDAX analysis was performed to investigate the chemical composition of the synthesized $Mg_{(1-x)}Mn_xCo_2O_4$ (where x = 0.0, 0.5 and 1.0) are shown in Fig.3. According to EDAX analysis Mg, Mn, Co and O were the major constituents of the samples an no any other peak is observed indicates pure of the desired material is high.

4. Conclusion

The manganese substituted magnesium cobaltites are prepared by simple sol-gel method with high purity and desired shape. The synthesized material with 33 nm in size. Palladium is supported on the synthesized material by solution reduction method. The 2% palladium supported on $Mg_{(1-x)}Mn_xCo_2O_4$are used as a catalyst for Heck coupling reaction of bromobenzene and styrene. It is observed the $Mg_{(1-x)}Mn_xCo_2O_4$is a better support for the palladium for Ecological heterogeneous catalyst. The 2% Pd/$Mg_{0.5}Mn_{0.5}Co_2O_4$shows better results as reported earlier.

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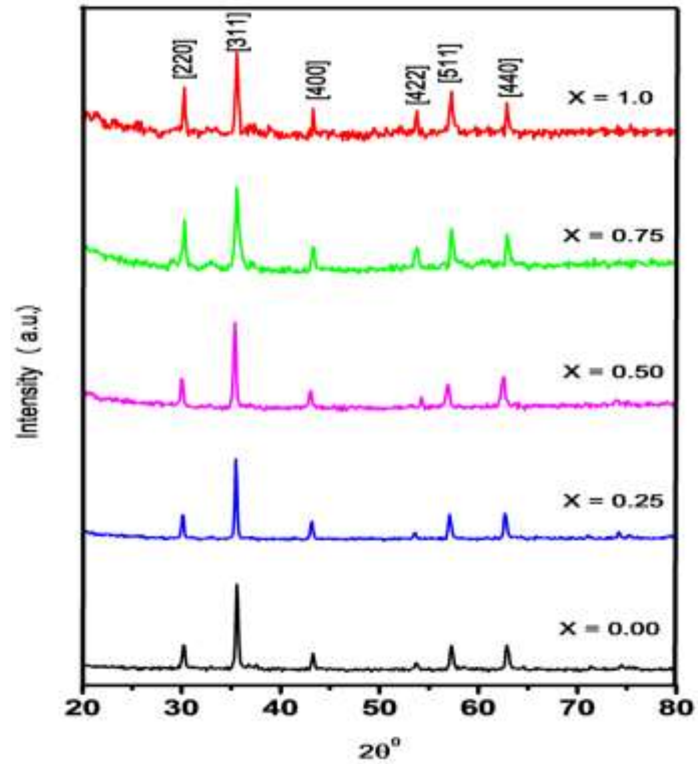
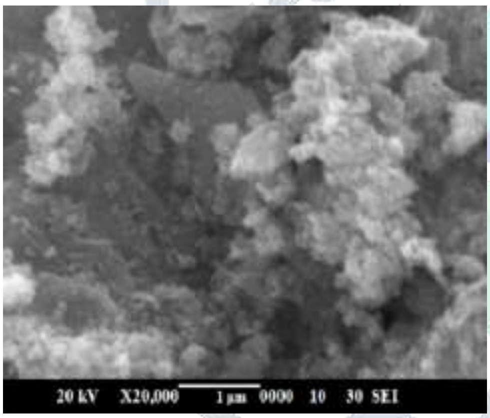
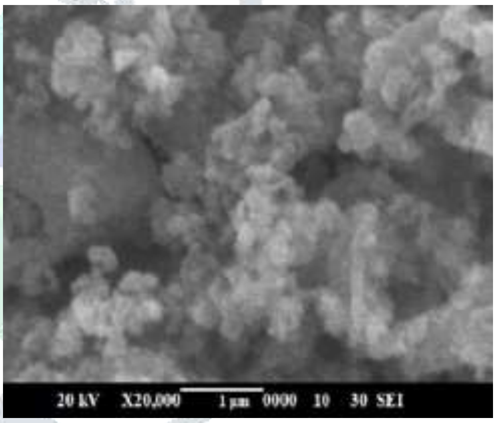
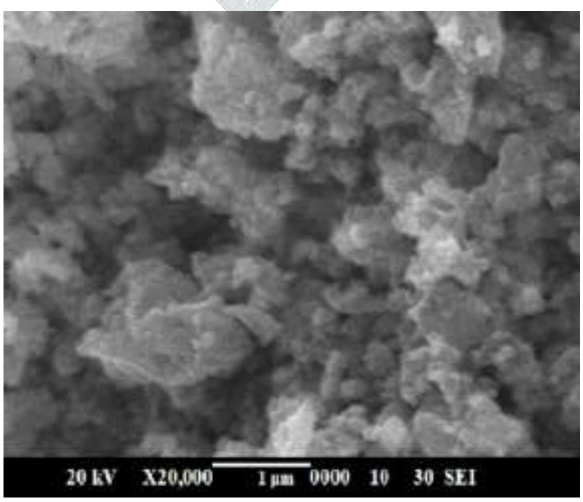


Fig. 1. XRD Patterns of $Mg_{1-x}Mn_xCo_2O_4$ ($0 \leq X \leq 1$).



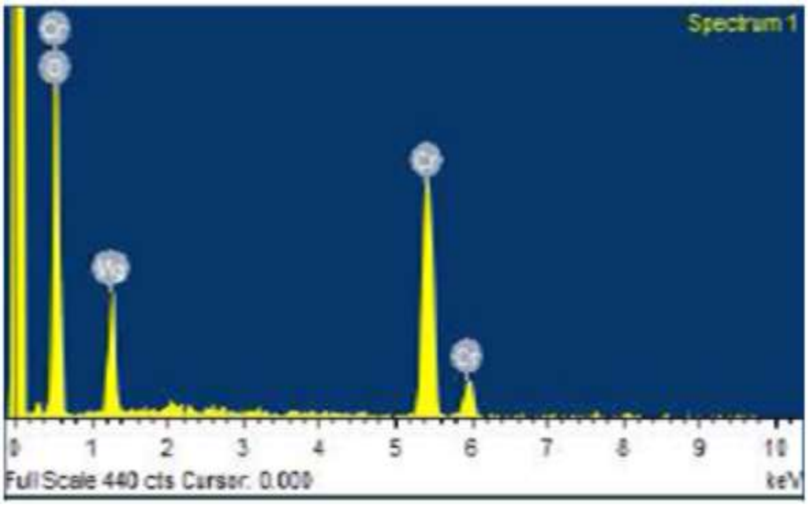


(a) **(b)**

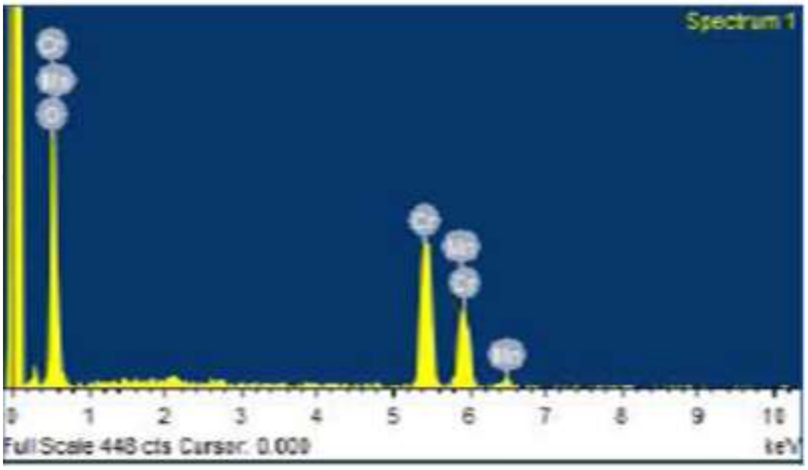


(c)

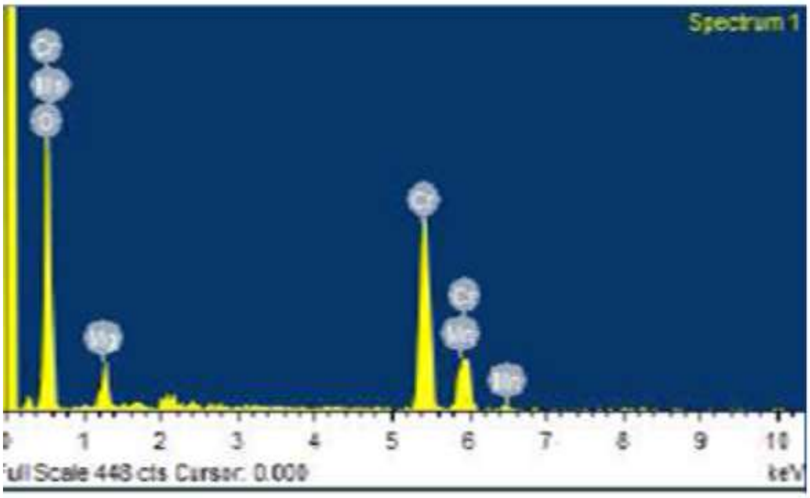
Fig. 2. Scanning Electron Micrographs of $Mg_{1-x}Mn_xCo_2O_4$,a) x =0.0, b) x= 0.5, c) x = 1.0



(a)



(b)



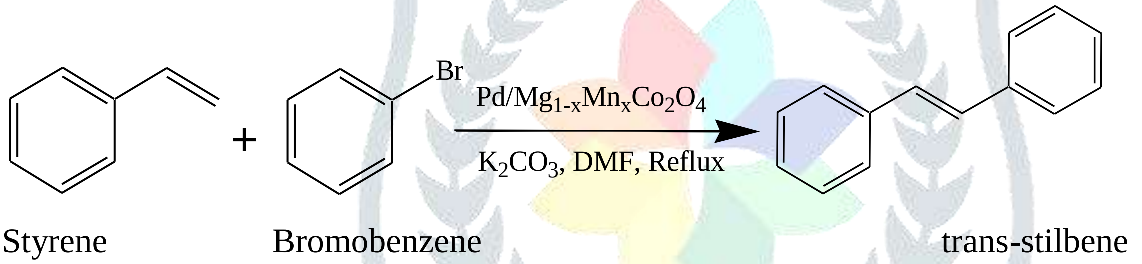
(c)

Fig. 3. Energy Dispersive Spectra of Mg_{1-x} $Mn_xCo_2O_4$,a) x =0.0, b) x= 0.5, c) x = 1.0

Table 1.Lattice constants, Crystallite size and X–ray density for $Mg_{1-x}Mn_x Co_2O_4 (0 \leq X \leq 1)$.

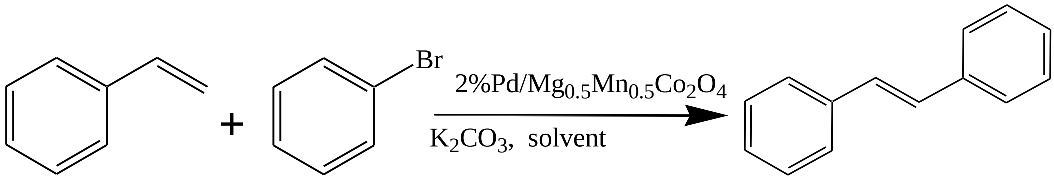
Sr.No.	Compound	Lattice Constants (Å)	Crystallite Size (nm)	X – ray density (d_x) g/cm^3
1	x = 0.0	8.197	34.41	3.72
2	x = 0.25	8.214	34.46	3.87
3	x = 0.5	8.221	34.62	3.89
4	x = 0.75	8.227	34.93	4.12
5	x = 1.0	8.238	35.14	4.27

Table 2. Effect of catalyst on Heck coupling reaction



Sr. No.	Catalyst	Conversion (%)
1	**$MgCo_2O_4$**	**54**
2	**$Mg_{0.75}Mn_{0.25} Co_2O_4$**	**61**
3	**$Mg_{0.5} Mn_{0.5}Co_2O_4$**	**68**
4	**$Mg_{0.25} Mn_{0.75}Co_2O_4$**	**65**
5	**$MnCo_2O_4$**	**65**

Table 3.Effect of temperature on Heck coupling reaction



Styrene Bromobenzene trans-stilbene

Sr. No.	Temperature	Yield (%)
1	60	35
2	70	39
3	80	43
4	90	57
5	100	68
6	110	69