

Catalytic Activity Studies of Modified Alumina in the Esterification of Benzyl Alcohol with Different Aliphatic Acids

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A varied percentage of Fe, Co and Fe-Co mixtures were deposited on alumina support by dry impregnation method. The prepared materials were analyzed for their crystallinity, surface functional groups, morphology and elemental composition by P-XRD, FT-IR, and SEM-EDS techniques. Specific surface area of the catalytic materials was determined by BET technique using nitrogen as adsorbent. Further, surface acidity was estimated by TPD-NH₃ and *n*-butylamine back titration method. The catalytic performances of these materials were checked in the esterification of benzyl alcohol with various aliphatic acids. The catalytic activity of Fe-Co/Al₂O₃ with 15% metal loading was found to be superior to other catalysts. The higher catalytic performance of the catalyst may be attributed to the higher surface acidity as well as synergetic effect of the metals. Further, the catalyst Fe-Co/Al₂O₃ (15%) was recyclable up to 5 times with negligible loss of its catalytic activity. A close relationship was noticed between surface acidity and catalytic performance of the materials.

Keywords: Alumina support, Esterification, Benzyl alcohol, Reusable catalyst

Introduction

Acid catalyzed esterification of carboxylic acids and the acylation of alcohols are the fundamental synthetic organic reactions. The products aliphatic and aromatic esters find applications in various manufacturing industries, solvents, flavors, perfumeries, plasticizers, pharmaceuticals and agrochemicals¹⁻³. Acid catalysts are used in esterification reactions both in heterogeneous and homogeneous conditions. Generally industries use homogeneous catalysts such as acids like sulphuric acid, hydrochloric acid & hydrogen fluoride as well as organic acids like p-toluenesulfonic acid, chlorosulfonic acid to carry out esterification reactions. Even though homogeneous acids are effectual, they are corrosive, toxic and also product separation is a major problem due to contamination of the reaction mixture⁴⁻⁵. The use of heterogeneous solid catalysts in organic transformation reactions proposes many advantages over homogeneous catalyst such as higher selectivity, mild reaction conditions, simplified product isolation and reusability of the catalyst⁶⁻⁸. In heterogeneous

catalysis solid supports like clays, zeolites, transition metal oxides, alumina and resins are extensively used in the synthesis of fine chemicals, due to their unique beneficial catalytic properties and separation applications⁹⁻¹². Alumina (Al₂O₃) is a widely used solid support in heterogeneous catalysis for various reactions. The advantages of alumina include non-corrosiveness, less toxic, economic and easy separation of the catalytic material¹³⁻¹⁵. As reported in the literature, metal oxide and anion modified alumina are used in many catalytic applications. Gary H. P *et al*¹⁶ reported alumina catalyzed nucleophilic opening of structurally different epoxides using amines, acetic acid, alcohols, thiols, and benzeneselenol under mild conditions. Sarvari M. H and his coworkers¹⁷ reported, nitration of phenols and anilines by using alumina-sulphuric acid as a catalyst and Mg (NO₃)₂·6H₂O as nitrating agent. Campelo J.M and his team¹⁸ used Al₂O₃ and AlPO₄-Al₂O₃ catalysts for isomerization of cyclohexene in a microcatalytic pulse reactor. Narayan S¹⁹ *et al* have synthesized Co & Ni supported Al₂O₃ catalysts by co-precipitation method and used for aniline hydrogenation to obtain cyclohexylamine. Praliaud and his co-workers²⁰ have selectively reduced nitric oxide to nitrogen in presence of propane using Cu-ZSM5 and

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Cu/Al₂O₃ as a catalysts. It is note worthy that, various modified forms of Al₂O₃ catalyst support was also employed in different acid catalyzed esterification reactions.

For instance, Nagasawa K *et al*²¹ reported esterification of *tert*-butanol with acid chlorides or acid bromides using activated basic alumina as catalyst. Further the same group has synthesized *tert*-butyl esters from aliphatic acid chlorides by using activated alumina as a catalyst²². Niasari M. S. *et al*²³ used alumina supported metal chlorides of In, Ga, Fe, Zn, Cu, Ni, Co and Mn catalyst for the selective esterification of *tert*-butanol with acetic anhydride. Further several researchers have used Fe, Co catalyst supported on Al₂O₃ in the synthesis of organic fine chemicals. For instance, Reshetenko T. V²⁴ *et al* have prepared Fe/Co/Al₂O₃ catalyst by coprecipitation method and efficiently used it in decomposition of methane. Sardar A *et al*²⁵ have synthesized Fe, Co and a mixture of Fe & Co nanoparticles supported on alumina and found that bimetallic catalyst was highly efficient in the conversion of CO into hydrocarbons in Fischer-Tropsch reaction. Keeping in view the importance of iron, cobalt and alumina as catalysts in the synthesis of fine chemicals; we have deposited varied amounts of Fe, Co and Fe/Co mixture on Al₂O₃ and characterized by different analytical techniques. Subsequently, the catalytic activity studies were made using these catalysts in the esterification of benzyl alcohol with different aliphatic acids. The reaction conditions were optimized to get good yield of the product and the reusability of the catalyst was also investigated.

Experimental

Materials and Methods

Al (OH)₃ was obtained from SD fine chemicals, Mumbai, India. Fe(NO₃)₂ · 9H₂O, Co(NO₃)₂ · 6H₂O, acetic acid, propionic acid, butyric acid, pentanoic acid and benzyl alcohol of A.R grade were obtained from Merck specialties Pvt. India Ltd.

Preparation and characterization of the catalysts

Dry impregnation technique was used to prepare Fe, Co and Fe-Co mixtures supported on alumina by the following procedure. For instance, to prepare 1% Fe-Co/Al catalyst, 0.72 g of Fe (NO₃)₂ · 9H₂O & 0.49 g of Co (NO₃)₂ · 6H₂O were weighed accurately and mixed well in a mortar & pestle. To this powdered salt, 1mL of distilled water was added to get homogenized salt solution. 19.80 g Al(OH)₃ powder

was added to the salt solution, mixed well and dried in an air oven at 110 °C for 12 h. The sample is represented as uncalcined catalyst. Similarly 1, 5, 10, 15 wt. % of Fe, Co or mixture of the two salts and the remaining weight percent as Al(OH)₃ in the different catalytic materials were prepared. Further these samples were calcined at 550 °C in a muffle furnace for 6 h and are represented as calcined catalysts. The prepared catalysts were characterized by different analytical techniques. Powder X-ray diffraction (P-XRD) patterns were recorded on a Panalytical Xpert pro X-ray diffractometer using Cu K α radiation (λ = 0.154 nm) in the 2 θ range of 5° to 70° at 40 kV and a scanning rate of 2 °min⁻¹. Fourier Transform-Infrared spectroscopy (FT-IR) spectra were recorded from a Nicolet Model Impact 400D FT-IR spectrometer with 4 cm⁻¹ resolution by KBr pellet technique. Brunauer Emmett and Teller (BET) surface area was determined from N₂ adsorption data acquired on a Micromeritics TriStar 3000 instrument. The surface acidity was estimated by using Mayura analytical Temperature- Programmed Desorption- Ammonia (TPD-NH₃) analyzer and in addition to *n*-butyl amine back titration method²⁶. Morphology and the elemental composition of the catalytic materials were determined by scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) technique using Quanta 200 FEI instrument. The characterization for the samples with 15% of Fe, Co and Fe/Co on Al (OH)₃ has been discussed in detail further in the text, as these catalysts gave higher % yield of the products than the other catalysts. These catalytic materials are abbreviated as Fe/Al, Co/Al and Fe-Co/Al respectively for 15% Fe, Co and Fe/Co loaded on Al(OH)₃.

Catalytic activity

The catalytic activity of all the prepared catalysts were investigated in an acid catalyzed esterification of benzyl alcohol with different aliphatic acids such as acetic acid, propionic acid, butyric acid and pentanoic acid (valeric acid). In a typical procedure a mixture of benzyl alcohol and an aliphatic acid in 1:1 molar ratio was refluxed with 200 mg of catalyst in a 100 mL R B flask. After a definite period of time, the reaction mixture was cooled to room temperature and filtered to separate the solid catalyst. The isolated products were analyzed by GC (Shimadzu gas chromatography with 2 m stainless steel packed column with 10% RTX Stabilwaxsilcoport) using 1,4 dioxane as an internal standard. The reaction was also carried out

without the addition of catalyst and gave a negligible amount of the expected product. Only in presence of catalyst, % yield of the product was increased. Further optimization of the reaction conditions were carried out to obtain respective esters.

Results and Discussion

Characterization of the catalysts

The X-ray diffraction patterns of calcined Fe/Al, Co/Al and Fe-Co/Al catalysts are given as supplementary data. From the P-XRD patterns of the catalytic materials, Fe/Al shows well defined diffraction peaks at 2θ values of 31.1° , 36.9° and 65.1° corresponding to the reflections from the (4 0 0), (2 2 1) and (2 4 0) planes. These peaks are the characteristic diffraction patterns of the Al_2O_3 ²⁷⁻²⁸. After impregnating Fe into the Al_2O_3 matrix, new diffraction peak was observed at 2θ value of 44.6° corresponds to (1 1 0) plane of Fe in Fe/Al²⁹. In P-XRD pattern of Fe-Co/Al catalyst, diffraction peaks at 2θ values 29.7° , 36.2° , and 42° corresponds to the (2 1 2), (1 3 1) and (1 1 5) planes respectively for Al_2O_3 ³⁰. However the diffraction peak for Fe at 2θ value 44.6° corresponding to (1 1 0) plane of Fe is not observed in Fe-Co/Al. The other predominant peak at 2θ value of 61.2° corresponds to (1 0 1) plane of Co³¹. Further observation was that, Fe-Co/Al is more crystalline than the other two catalysts on calcination at 550°C . The crystalline nature of Fe-Co/Al is also evident from SEM images. Co/Al seems to appear as amorphous solid as there are no intense sharp peaks and may possess highly dispersed X-ray amorphous phases. FT-IR spectra of calcined samples of Fe/Al, Co/Al and Fe-Co/Al are given in supplementary data. All the three prepared catalysts show broad bands around $3440\text{--}3450\text{ cm}^{-1}$ and $1639\text{--}1653\text{ cm}^{-1}$ which are due to the stretching and bending vibrations of the hydroxyl groups respectively. The weak absorption bands at 1082 and 1063 cm^{-1} in all the three catalysts are attributed to Al-O-Al bonds²⁴. In addition to these absorption bands, Fe/Al catalyst exhibited absorption band at 563 cm^{-1} which is due to the Fe-O stretching vibrations. In Co/Al catalyst the two distinct absorption peaks at 669 and 550 cm^{-1} are due to characteristic Co-O stretching vibrations. In case of the Fe-Co/Al catalyst, the absorption bands at 649 and 530 cm^{-1} are shifted from the original absorption bands which correspond to Co-O stretching vibrations³². However the Fe-O stretching vibration band at 563 cm^{-1} is not observed in Fe-Co/Al. Here it may be presumed that the interactions of metal ions

with the support Al_2O_3 is distinctly different in each case. SEM images and EDS profiles of all three calcined catalysts are represented in Figure 1. In SEM image analysis of Co/Al catalyst, it was observed that the particles are uniformly deposited on the support in the form of spheres. Further in Fe/Al catalyst, particles are irregular in shape with larger size in comparison with Co/Al catalyst. The SEM image of Fe-Co/Al catalyst revealed more crystalline particles which is also evident from XRD pattern. The elemental composition of the three catalysts indicated the presence of respective elements in different catalysts with atomic weight percentage. BET surface area and surface acidity values of the three catalysts are given in Table 1. It is clear that surface area of Co/Al is higher than Fe/Al and Fe-Co/Al. The order of surface acidity is Fe-Co/Al > Fe/Al > Co/Al. In heterogeneous catalysis it is not only that the surface area of the catalyst is important but also the type of Lewis acidity or basicity which would enhance the catalytic activity for a particular reaction. This selected organic reaction requires more number of Lewis acid sites. The catalyst Fe-Co/Al with highest acidity and lowest surface area among the other two catalysts gives highest catalytic activity as discussed further in the text. When the catalysts were subjected to TPD- NH_3 desorption studies in the temperature range from 50 to 600°C , the amount of ammonia desorbed by the catalytic materials are represented in Figure 2. According to literature, the desorption peaks obtained at different temperatures indicate the presence of weak, strong and intermediate acid sites. The desorption peaks obtained in the range $50\text{--}250^\circ\text{C}$ is credited for the weak acid sites, $250\text{--}350^\circ\text{C}$ for moderately strong acid sites. The desorption peaks obtained at more than 350°C is for very strong acid sites³³. From the TPD- NH_3 profiles it is noteworthy that, Fe-Co/Al showed a strong desorption peak in the range $350\text{--}450^\circ\text{C}$ which is due to the existence of strong acid sites.

Catalytic activity

Liquid phase esterification reactions of benzyl alcohol with different aliphatic acids were carried out in the presence of Fe/Al, Co/Al and Fe-Co/Al catalysts. Both calcined and uncalcined catalysts were used in esterification reactions of benzyl alcohol with aliphatic acids. In general, it was noticed that the % yield of the esters obtained using calcined catalysts was much higher than uncalcined catalysts irrespective of raise in temperature, duration and

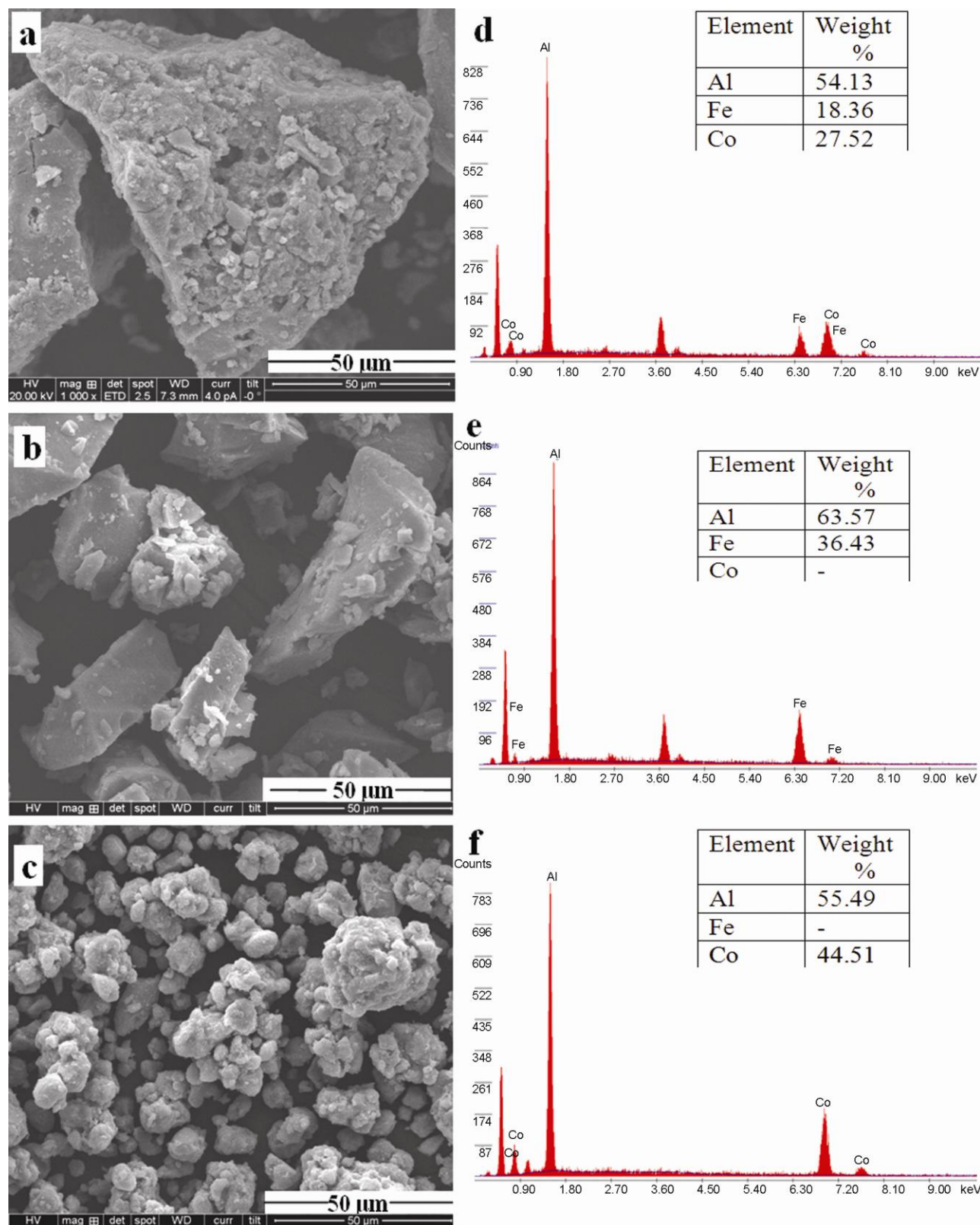
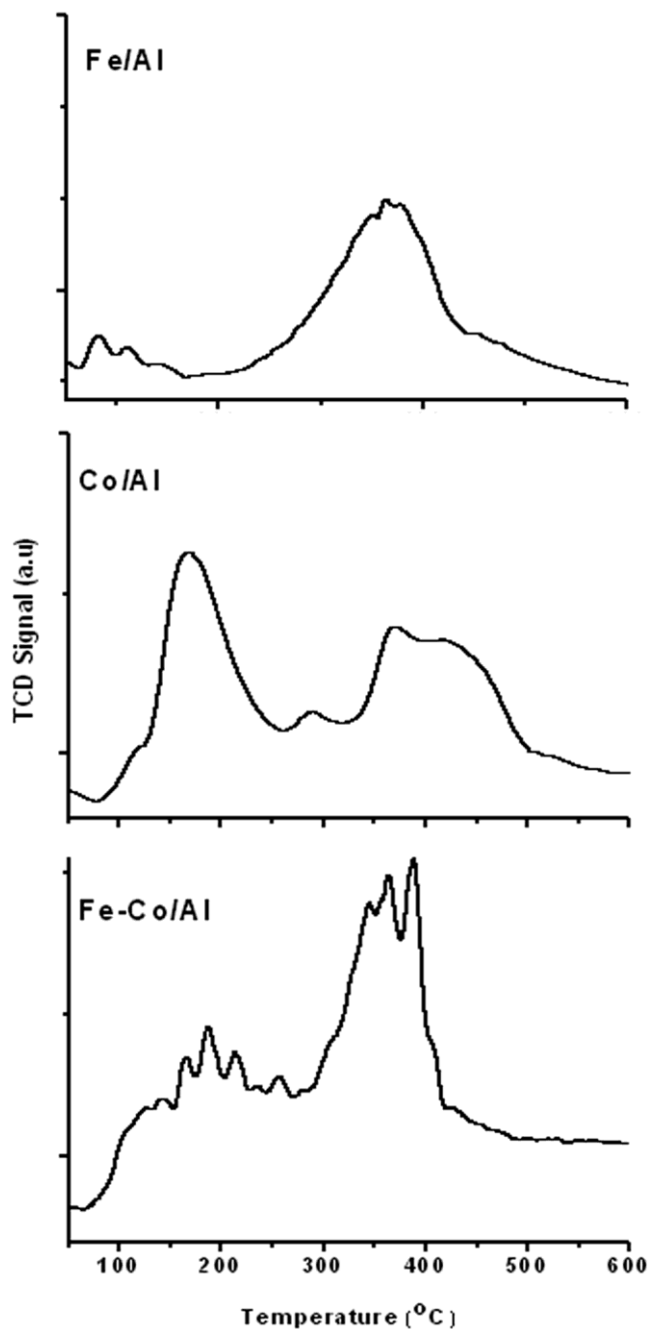


Fig.1—SEM images of the catalysts Fe-Co/Al, Fe/Al and Co/Al (a, b, c) and their corresponding EDS profiles (d, e, f)

Table 1—BET surface area and surface acidity of Fe/Al, Co/Al and Fe-Co/Al

Catalysts	Surface Area (m^2g^{-1})	Surface acidity (mmolg^{-1})
Fe/ Al	131.6	6.65
Co/ Al	135.3	3.85
Fe Co/Al	117.6	7.16

Fig.2—TPD- NH_3 profile of the catalysts Fe/Al, Co /Al and Fe-Co/Al

amount of the catalysts used. Hence it is presumed that when the catalysts were calcined at 550°C , higher concentrations of catalytically active stronger acid sites are generated which leads to higher % yield of the product. Another observation was that, as the % loading of the metal/s on Al_2O_3 increases, the catalytic performance of the catalysts increases in the esterification of benzyl alcohol with different aliphatic acids. Based on these results, the catalytic activity of Fe/Al, Co/Al and Fe-Co/Al (with 15% metal loaded) catalysts were studied in the esterification reaction of benzyl alcohol with different aliphatic acids such as acetic acid, propionic acid, butyric acid and pentanoic acid (Table 2) in different reaction conditions. The catalytic reactions were carried out using these catalysts at 90°C , 110°C , 130°C and 150°C and a maximum % yield of the esters were obtained at 130°C . The order of catalytic activity of all the catalysts in the esterification of benzyl alcohol with different aliphatic acids is acetic acid > propionic acid > butyric acid > pentanoic acid. This decreasing trend in carboxylic acid reactivity with increasing alkyl chain length is attributed to inductive effect and steric hindrance³⁴ which slows down the esterification reaction. Here as methylene moiety increases in different aliphatic carboxylic acids, inductive effect plays an essential role in releasing electrons from respective carboxylic acids and hence the decreasing affinity for electrons in carbonyl carbon atom. Steric effect is another important concept to be considered in this esterification reaction. As the esterification reaction is a reversible reaction and the byproduct obtained is water, it is required to remove water from the ester as and when formed. If water molecule is not removed the reversible reaction may proceeds leading to less % yield of esters. From Table 2 it is clear that 15% Fe-Co/Al catalyst exhibited an excellent catalytic activity in the formation of the different esters with 100% selectivity, while Co/Al exhibited lowest activity in acid catalyzed esterification reactions. This is attributed to higher surface acidity of Fe-Co/Al catalyst and the synergetic effect of the two metals. Further optimization of the reaction conditions for the esterification of benzyl alcohol with only acetic acid in the presence of calcined 15% Fe-Co/Al, Fe/Al, Co/Al catalysts was carried out by changing the duration of the reaction, temperature, amount of catalyst and molar ratios of the reactants. The % yield of isolated ester was examined by varying reaction

Table 2—Catalytic activity of Fe/Al, Co/Al and Fe-Co/Al catalysts in the esterification of benzyl alcohol with different carboxylic acids such as acetic acid, propionic acid, butyric acid and pentanoic acid

Sl. No	Catalysts	Duration of the reaction (h)	Benzyl acetate yield at 130 °C (%)	Benzyl propionate yield at 130 °C (%)	Benzyl butyrate yield at 130 °C (%)	Benzyl pentanoate yield at 130 °C (%)
1	Without Catalysts	8	17	15	12	9
2	Fe/Al	2	43	39	36	31
	Fe/Al	4	58	47	38	35
	Fe/Al	6	66	56	47	39
	Fe/Al	8	74	63	56	43
	Fe/Al	24	81	70	70	56
	Fe/Al	48	86	79	72	61
3	Co/Al	2	42	35	31	28
	Co/Al	4	49	44	37	31
	Co/Al	6	55	53	44	36
	Co/Al	8	62	62	55	42
	Co/Al	24	73	68	62	48
	Co/Al	48	80	72	65	52
4	Fe-Co/Al	2	46	39	36	31
	Fe-Co/Al	4	57	54	51	50
	Fe-Co/Al	6	68	65	58	53
	Fe-Co/Al	8	79	69	59	54
	Fe-Co/Al	24	86	78	64	58
	Fe-Co/Al	48	96	86	74	63

* The obtained products in these reactions were analyzed by gas chromatography and internal standard used was 1, 4- Dioxane.

time from 2 to 48 h over 15% metal/s loaded Al_2O_3 catalysts. The obtained results are presented in Table 2. The % yield of the ester was enhanced with increase in time and reached maximum at 48 h, this trend was observed in all the catalysts. A highest % yield of the products was obtained in Fe-Co/Al catalyst. The reaction was carried out by varying the reaction temperature from 90-150 °C over 15% metal/s loaded Al_2O_3 catalysts for 48 h. The obtained results are shown in Figure 3a. The % yield of benzyl acetate was found to increase with the reaction temperature. It indicated that higher reaction temperature favors the formation of ester. When the temperature was increased above 130 °C it showed less progress in the increase of percentage yield of ester. Therefore, the reaction temperature of 130 °C was chosen as a suitable reaction temperature for further optimization of other reaction conditions. In order to find out the effect of the amount of the catalysts on % yield of benzyl acetate, the amount of catalysts was varied from 0.1g to 0.4 g and using 1:1 molar ratio of benzyl alcohol: acetic acid as given in Figure 3b. The reaction was carried out at 130 °C for

48 h. when 0.2 g of the catalyst was used higher % yield of the product benzyl acetate was obtained. As the amount of the catalyst increased from 0.2 g to 0.3 g the % yield of the product remained constant. Further increasing the amount of the catalyst from 0.3 g to 0.4 g the % yield of the product slightly decreased. It is understood that, as the amount of the catalyst increases number of active sites also increases. Since it is a reversible reaction, the rate of backward reaction may be enhanced when amount of the catalyst was more than 0.3 g and eventually decreasing in the % yield of the benzyl acetate. Thus 0.2 g is an optimum amount of catalyst required for this esterification reaction. The reaction was carried out over 15% metal/s loaded Al_2O_3 catalysts using different molar ratios of acetic acid and benzyl alcohol (1:3, 1:2, 1:1, 2:1, 3:1) as given in Figure.3c. In all cases, only benzyl acetate was formed as a product. It is noteworthy that % yield of product was found to be higher in 1:1 molar ratio of benzyl alcohol and acetic acid in presence of Fe-Co/Al in comparison with Fe/Al and Co/Al catalysts.

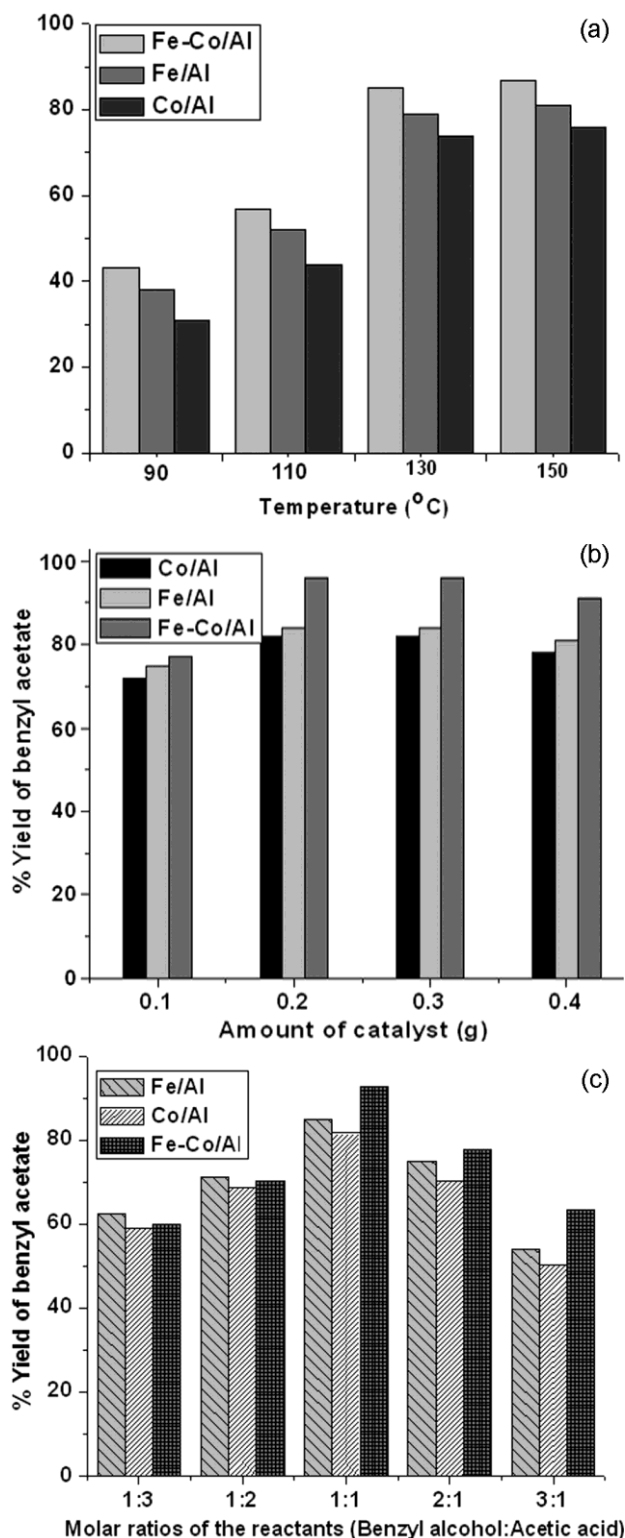


Fig.3—Catalytic performances of Fe-Co/Al, Fe/Al and Co/Al catalysts in the esterification of benzyl alcohol with acetic acid a) effect of temperature b) different amount of the catalysts and c) different molar ratios (benzyl alcohol: acetic acid) of the reactants.

Reusability of the catalysts

To study the reusability of the Fe-Co/Al catalyst, after the catalytic activity test the catalyst was separated by simple filtration and thoroughly washed with distilled water several times. Finally the catalyst was washed with acetone and dried at 110 °C for 12 h. Thus obtained catalyst was reused for 4 times in esterification of benzyl alcohol with acetic acid under similar reaction conditions. Until 3 repeated cycles the % yield of the ester remained constant, in 4th & 5th cycle the yield of ester was slightly decreased (Table 3). This may be due to partial leaching of acid sites which do not strongly adhere to the surface of Al₂O₃.

Mechanism of esterification reaction

Figure 4 shows a plausible reaction mechanism for the esterification of benzyl alcohol and different aliphatic acids in the presence of Fe, Co and Fe-Co supported on alumina for the synthesis of corresponding ester. Initially, an acidic site of the catalyst reacts with oxygen of carbonyl group of different aliphatic acids forming intermediate A.

Table 3—Reusability of Fe-Co/Al catalyst (0.2 g of catalyst, for 48 h at 130 °C) in the esterification of benzyl alcohol to benzyl acetate

No of cycles	% Yield of benzyl acetate
1	96
2	96
3	95
4	94
5	93

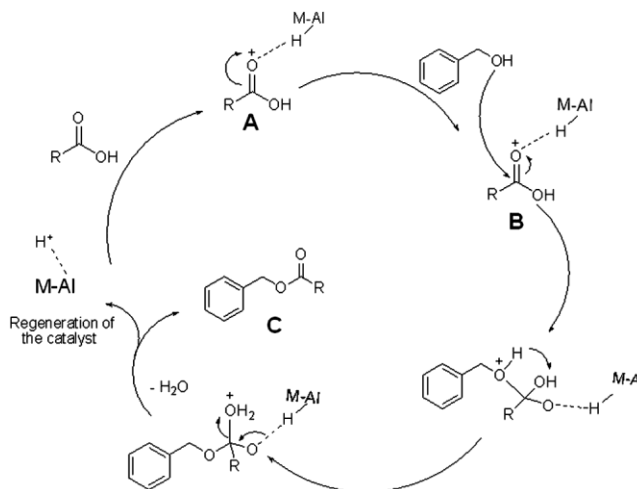


Fig.4—A Possible reaction mechanism for the esterification of benzyl alcohol with different acids by using Fe/Al, Co/Al and Fe-Co/Al catalysts

Protonation of the carbonyl oxygen by acidic catalyst makes the carbonyl carbon a much better electrophile, which reacts with benzyl alcohol forming intermediate B. As the reaction proceeds, corresponding ester C is obtained along with a water molecule and the catalyst is regenerated.

Conclusions

The catalytic activities of Fe/Al, Co/Al and Fe-Co/Al catalysts were investigated in the esterification reactions of benzyl alcohol with different aliphatic acids. The order of catalytic activity was found to be Co/Al < Fe/Al < Fe-Co/Al irrespective of the percentage loading of the transition metal/s on alumina, temperature and duration of the reaction. However as the percentage loading of transition metal/s on alumina was increased, the catalytic activity was found to be higher. 15% loaded Fe-Co/Al with higher acidity showed good catalytic activity for the synthesis of respective esters using different aliphatic acids with benzyl alcohol. The order of reactivity of different aliphatic acids with benzyl alcohol was found to be acetic acid > propionic acid > butyric acid > pentanoic acid. Here we conclude that, increase in the carbon chain of aliphatic acids has decreased their reactivity which is due to inductive effect and steric hindrance. The reaction between benzyl alcohol and acetic acid using Fe-Co/Al gave highest % yield of the benzyl acetate (96 %). This catalyst was reused up to 5 times without losing its catalytic activity and proved to be an efficient, recyclable, economical and environmentally benign catalyst.

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