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Fridel-Crafts benzylation over transition metal oxides supported on ceria

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ABSTRACT

Liquid phase benzylation of benzene with benzyl chloride (BC) were carried out in presence of Iron doped ceria nanocatalyst prepared by hydrothermal technique. The Fe-ceria was very active benzylation catalysts with almost 100% selectivity to monoalkylated product and showed good stability. The significance of the catalyst was recovered and reused for the benzylation of benzene for several times.

Keywords: Hydrothermal method, benzylation, Solid acids, liquid phase.

INTRODUCTION

Fridel-Crafts alkylation reaction was generally used for the synthesis of diphenylmethane (DPM). The liquid phase benzylation of benzene and other organic compounds using benzyl chloride as alkylating agent gives diphenylmethane and substituted diphenylmethane product which are industrially important used in the fine chemicals [1] as well as pharmaceutical intermediates [2]. The diphenylmethane derivatives possess biological importance, used as monomers in macrocycles, catenanes and rotaxanes [3,4]. In the fragrance industry diphenylmethane has been used as both a fixative and a scenting soap, as a synergist in some insecticides [5,6] and as a plastisizer [7] for dyes [8].

A number of reviews are available on the liquid phase and gas phase Fridel-Craft reaction using solid acids in general as catalyst [9-18]. Generally for the Fridel-Crafts alkylation reaction mineral acids like HF, H_2SO_4 and Lewis acids like BF_3, $AlCl_3$ was used but such catalysts produces toxicity, environmental pollution difficult to separation from the reaction mixture and recovery of the catalysts. To avoid such drawbacks they are replaced by using solid acid catalysts which are non-corrosive, pollution free, reusable and produce good catalytic activity in the Fridel-Crafts reaction. Heterogeneous catalysts have proved to be central to this strategy, and the careful control of the reactions can maximize the selectivity and yield of a single desired product, while minimizing the formation of by-products. The use of solid acid catalysts as non-conventional Fridel-Crafts catalysts, instead of the hazardous mentioned catalysts, is very interesting from both the environmental and economic points of view. Development of reusable solid acid catalysts having high activity with little or no moisture sensitivity for the liquid phase Fridel–Crafts type reactions is therefore of great practical importance.

Reaction rates as well as mechanism are affected with structure of alkylation agent, polarity, solvatation ability of solvent and nature of catalyst.

V.R. Choudhary et al [19] has studied that benzylation of benzene by benzyl chloride over Fe, Zn, Ga and In modified ZSM-5 type of catalysts and Ga, In modified H-β type of catalysts, higher activity for the Ga, In-modified Zeolites assigned to the redox properties of the catalysts. He et al. investigated the catalytic performance of iron supported mesoporous materials for the alkylation of benzene with benzyl chloride [20]. Sugunan et al. studied the catalytic performance of H-ZSM-5, H-beta, H-mordentite, H-Y catalysts etc. for the benzylation of o-xylene with benzyl chloride [21]. Advantages of alkylations in liquid phase are longer lifetime of catalyst and simply thermal

control of process [22]. Bachari et al. [23] studied the benzylation of benzene and substituted benzene employing benzyl chloride over a series of Cu containing mesoporous silica.

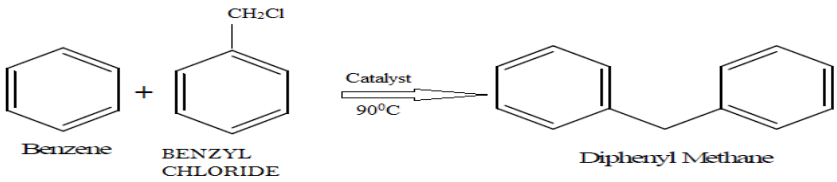
In present study transition metals supported on nanocrystalline ceria synthesized by using hydrothermal method. Characterization of the catalysts showed good surface properties reported in our earlier work [24], therefore these catalysts were used in the benzylation reaction. Among the prepared catalysts, iron supported on nanoceria gave higher selectivity as well as conversion in benzylation reaction. Fridel-Crafts benzylation of benzene and other aromatic compounds with benzyl chloride have been performed to obtain diphenylmethane and substituted diphenylmethane products under solvent free condition and various parameters such as catalyst amount, reaction time, reaction temperature, molar ratio of the reagents etc. In the catalytic activity catalyst plays synergic role in the reaction mechanism.

MATERIALS AND METHODS

All the materials used for the reaction were AR grade and purified. Chemicals Benzene (Merck), Benzyl Chloride (97%), Anisole (99%), Bromobenzene (99%), Chlorobenzene (99.8%), Toluene (99.8%) were purchased from Sigma Aldrich and used without purification. XRD was carried out on a Rigaku Miniflex X-ray diffractometer with Cu Kα-line radiation source (λ= 1.54178 A^0) scanning rate of 0.02^0/s was applied to record the pattern in the 2Θ range of 20- 80^0. Transmission Electron Microscopy (TEM, FEL TECNI G^2 20 ULTRA-TWIN) technique was conducted for the study the particle size as well as morphology of the particle. The BET surface area of the prepared catalyst was determined by N_2 sorption at -196°C using NOVA 1200 (Quanta Chrome) equipment. Prior to N_2 adsorption and evacuated at 300°C under vacuum condition. Acidity of the prepared catalysts was tested by using titrimetric method. GC-2014 Shimadzu used for the monitor the reaction samples having Flame Ionization Detector and Capillary column.

Catalytic studies

Liquid phase benzylation of benzene was done by using benzyl chloride in presence of prepared catalysts. The reaction was carried out in double necked 50 mL round bottom flask fitted with reflux condenser. In typical run, a mixture of benzyl chloride and benzene (1:6) along with the catalyst (0.2g) (activated upto 200^0c for 2 hrs) were taken in a round bottom flask and continuously stirred. The reaction was monitored by gas chromatography (GC-2014 Shimadzu) at regular intervals. After completion of the reaction, the catalyst was separated by filtration.



Regeneration of catalyst

During the course of the reaction, there is a probability of reacting molecules adsorbed on the surface of the catalyst. In the reaction mixture after separation of catalyst by decantation, it was first refluxed in ethanol for few minutes to solubilize and remove the adsorbed molecules, followed by drying and calcination. Finally the material was used as recycled catalyst. This regeneration process was followed in successive recycle reaction.

RESULTS AND DISCUSSION

4.1. Characterization techniques

4.1.1. X-ray Diffraction

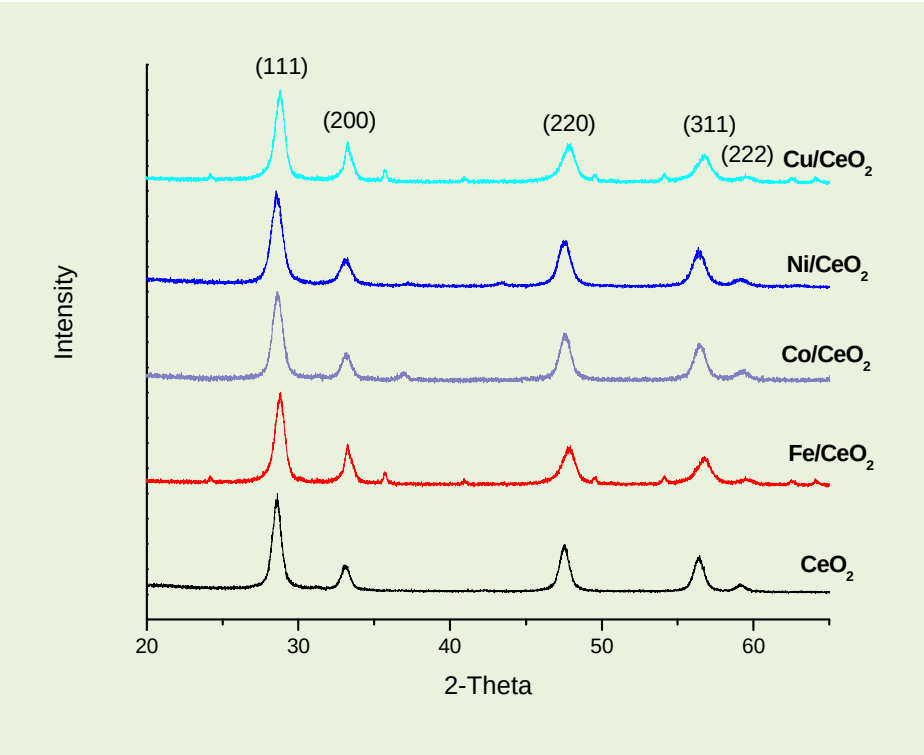
The X-ray diffraction patterns of prepared catalysts were showed in figure 1. Crystalline nature of all the materials was confirmed from the diffraction peaks. Formation of crystalline a single phase CeO_2 (JCPDS file 34-0394) has been confirmed from the XRD patterns of 773K calcined samples. The characteristic peaks corresponding to (111), (200), (220), (311) and (222) planes observed at 2θ = 28.83º, 33.2º, 47.9º, 56.7º and 59.4º respectively are very close to the face centered cubic CeO_2 crystal which indicating that all samples can be identified to ceria with the cubic fluorite structure. The crystallite sizes of synthesized catalysts were calculated by using Scherrer formula;

$$t= 0.9\lambda/\beta\cos\theta$$

Where, t= Average crystallite size, λ= wavelength of X-rays, θ= the position of the reflection in XRD pattern in degrees, B= integral breadth of a reflection (in radians 2θ) located at 2θ and by using internal reference standard it was calculated.

The crystallite size of pure CeO_2 was about 17 nm but after addition of the metal content, the intense peak as well as crystallite size reduced which showed in table 1. The crystallite size was considerably reduced by the loading of metal oxide on ceria. Addition of metal oxide on ceria improved the dispersion of the particles. In Fe/CeO_2, Xrd pattern indicates only α-Fe_2O_3 phase which showed major characteristic peak at 33.2^0 and 35.7^0. Similarly Co_3O_4, NiO and CuO phases showed peak at 33.2^0, 43.3^0 and 33.4^0 respectively.

Figure 1. X-ray diffraction patterns of CeO_2, Fe/CeO_2, Co/CeO_2, Ni/CeO_2 and Cu/CeO_2 catalysts calcined at 500^0C



4.1.2.BET Surface Area

The Surface area of prepared catalysts was also measured by using BET method. The pure ceria show very low surface area as compare to other prepared catalysts. From the below table 1, it was concluded that after adding the metal to ceria, the surface area also increases. Addition of metals favors the creation of structural defects. The formation of structural defects in turn favors the increase of surface area.

From the BET surface area results proposed that the surface area of doped ceria catalysts strongly depend on the nature and loading of the promoter.

4.1.3.Transmission Electron Microscopy

The surface morphology and structural properties of the prepared catalysts are illustrated by TEM technique, shown in Figure 2. TEM is commonly applied for studying the nature and size of supported catalysts. Detection of supported particles is possible provided that there is sufficient contrast between particles of metal oxides and ceria as support. Applications of TEM to study the dispersion of supported oxides. From images it was observed that, the agglomeration of somewhat rectangular shaped nanoparticles has taken place. The average particle size ranged from 8-16 nm for different prepared catalysts was found as shown in the table 1. These results are in good agreement with data obtained from XRD peak broadening measurements.

4.1.4.Acidity measurement

The nature of active sites as well as its number and strength have versatile role in determining the conversion and selectivity of acid catalyzed reactions. So the determination of acid strength was necessary to understand the catalytic activity and selectivity. Acid strength of the ceria nano catalysts were measured by using titrimetric experiment. The pure CeO_2 catalyst showed the lowest acidic strength at 1.217 mmol/g indicating the presence of weaker acid strength. Addition of metal content to the ceria support by hydrothermal technique increased the acid strength of the catalyst which was showed in table 1, with respect to the acid strength. Among all the catalysts, Fe/CeO_2 catalyst showed the highest acid strength (3.143 mmol/g) which enhances the catalytic activity. Therefore from the acidity data, acidity played an important role in the catalysis.

Figure 2. TEM images of a) Fe/CeO_2, b) Co/CeO_2, c) Ni/CeO_2, d) Cu/CeO_2

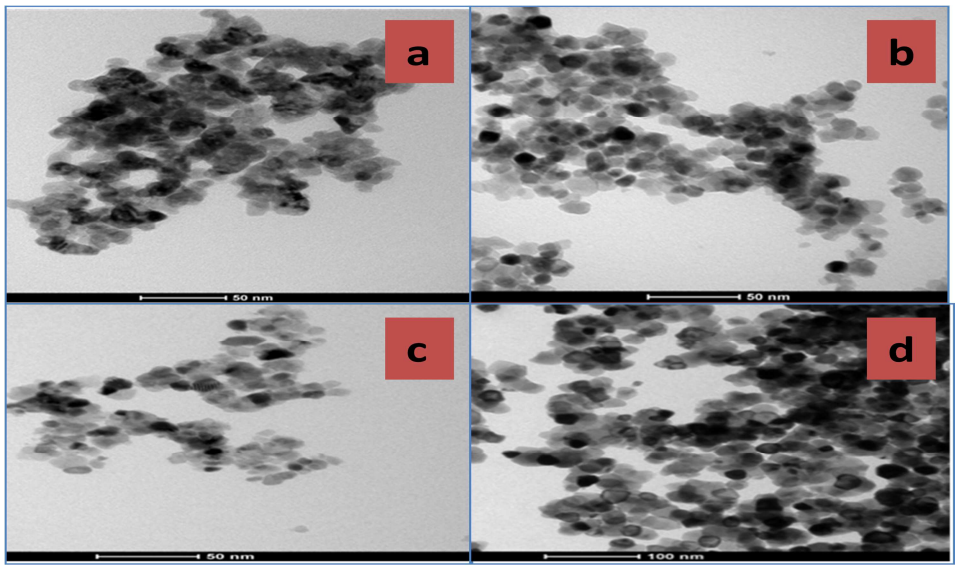


Table 1. Comparative data of XRD, TEM, BET surface area and acid strengths of prepared nanoceria catalysts

Sr. No.	Catalyst	Xrd (nm)	TEM(nm)	Surface area (m^2/g)	Acid strength (mmol/g)
1.	CeO_2	16.09	14-16	43	1.217
2.	Fe/CeO_2	10.39	9-12	55	3.143
3.	Co/CeO_2	10.00	9-11	105	2.500
4.	Ni/CeO_2	09.03	8-10	122	2.333
5.	Cu/CeO_2	16.48	13-16	130	2.900

4.2. Catalytic Studies

The present study deals with synthesis of diphenylmethane from benzylation of benzene with benzyl chloride as alkylating agent. Influence of various reaction parameters was studied. Lewis acid sites which are present on the surface of the catalysts were responsible for the alkylation activity.

Influence of reaction parameters

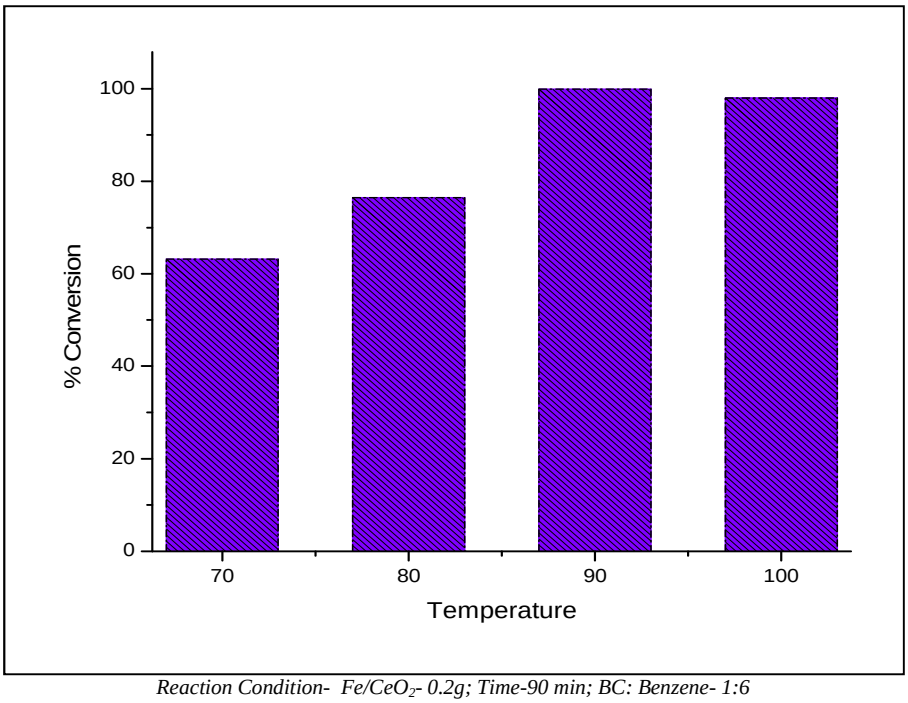
4.2.1.Effect of Temperature:

Influences of temperature on benzylation of benzene with benzyl chloride are illustrated in figure 3. Increase in temperature showed strong effect on both conversion and selectivity of diphenylmethane. Reactions were carried out at various temperatures. An increase in the conversion is achieved with an increase in reaction temperature. At 70^0C, 63% conversion of benzyl chloride was observed. When the temperature was increased from 70^0C to 90^0C, conversion of benzyl chloride also increases from 63% to 99.94%. Above 90^0C to 100^0C conversion of benzyl chloride slightly decreases but selectivity remains constant. The high reaction temperature favors the production of polymerized products. So the temperature 90^0C was selected for the further studies.

4.2.2.Effect of various catalysts

The prepared catalysts were tested on benzylation of benzene under solvent free condition. The effect of various catalysts on the benzylation of benzene reaction was studied and results are depicted in the table 2. Reaction was carried out without catalyst by keeping reaction parameters constant, it was observed that there was no reaction. In presence of pure ceria there was no conversion of benzyl chloride as well as selectivity observed. Among all the catalysts, Fe/CeO_2 catalyst showed good conversion of benzyl chloride and 100% selectivity of DPM. From results it is indicated that after addition of metal oxide on ceria the acidity of the catalysts increases. Therefore, Fe/CeO_2 showed highest acidity compared to other catalysts, which was responsible for the increase in conversion of benzyl chloride.

Figure 3. Effect of temperature on benzylation of benzene with BC



Reaction Condition- Fe/CeO_2- 0.2g; Time-90 min; BC: Benzene- 1:6

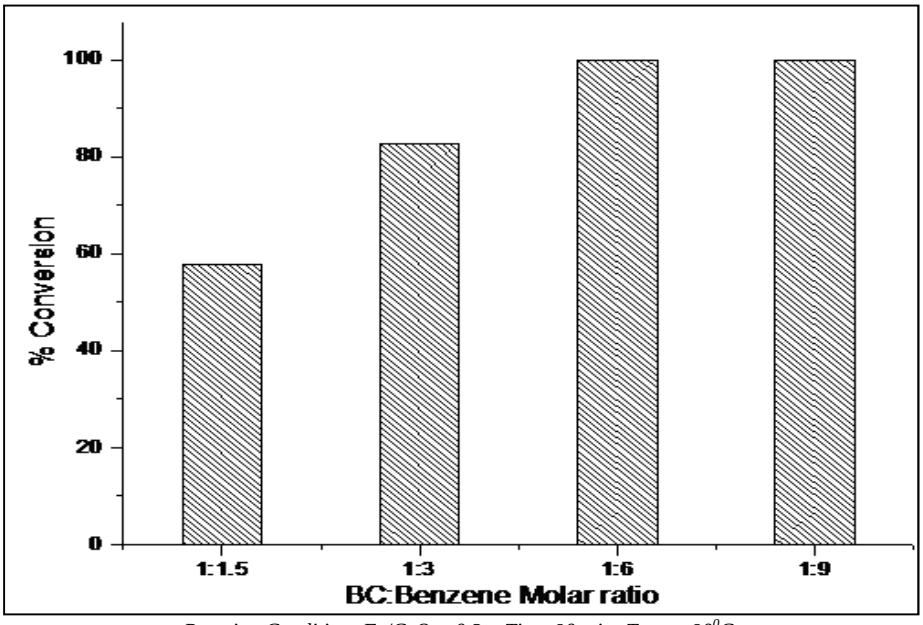
Table 2. Effect of various catalysts on benzylation of benzene with BC

Sr.No.	Catalyst	% Conversion of BC	% Selectivity of DPM
1.	Without catalyst	No Reaction	-
2.	CeO_2	No Reaction	-
3.	Fe/CeO_2	99.94	100
4.	Co/CeO_2	6.74	99.92
5.	Ni/CeO_2	4.67	99.98
6.	Cu/CeO_2	7.12	99.99

Reaction Condition- Catalyst- 0.2g; Time-90 min; Tempt.-90^{0}C; BC: Benzene- 1:6

4.2.3.Effect of BC/Benzene Molar ratio

Figure 4. Effect of BC/Benzene Molar ratio on benzylation of benzene with BC



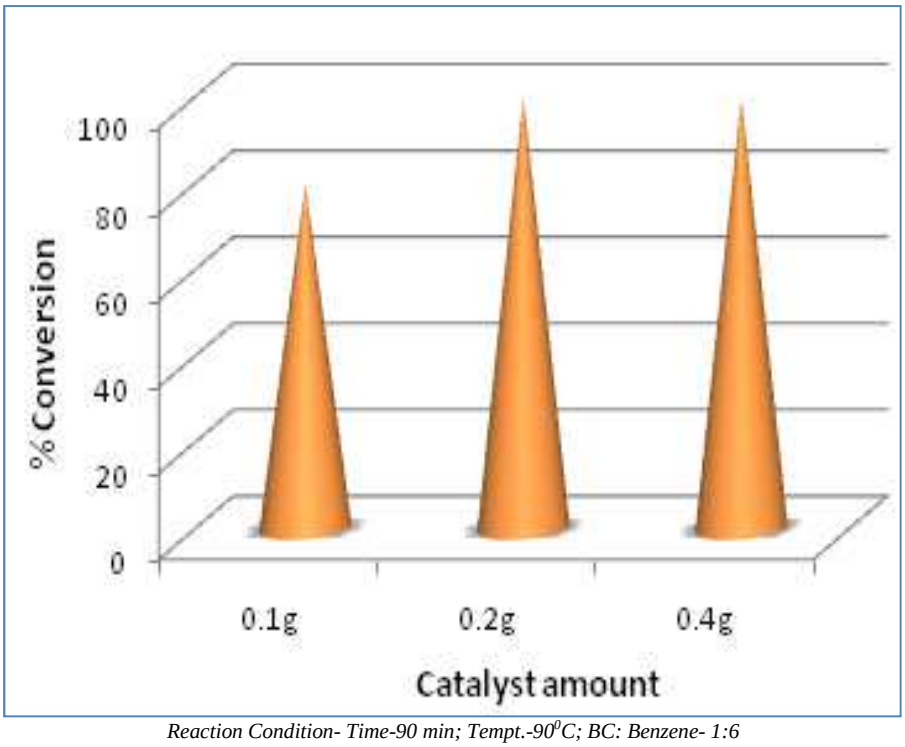
Reaction Condition- Fe/CeO_2 - 0.2g; Time-90 min; Tempt.-90^{0}C.

Benzyl chloride to benzene mole ratio was varied from 1:1.5 to 1:9, by keeping the temperature (90^0) and catalyst amount (0.2g) constant showed in figure 4. On increasing the concentration of benzene it was observed that, initial increase in the conversion was observed on increasing the amount of benzene from 1:1.5 to 1:6. However, further increase in the amount of benzene from 1:6 to 1:9 molar ratios, conversion slightly reduced. So for the further studies 1:6 molar ratio was selected.

4.2.4.Effect of Catalyst amount

The effect of catalysts amount on the benzylation of benzene with benzyl chloride was studied. The catalysts amount was varied between 0.100 to 0.400g by keeping the temperature (90^0C), mole ratio of BC to Benzene (1:6) constant showed in figure 5. A linear increase in the rate of benzyl chloride conversion with time was observed. On increasing the catalyst amount, conversion also increases. Due to availability of Lewis acid sites in catalyst improve the catalyst activity.

Figure 5. Effect of catalyst amount on benzylation of benzene with BC



Reaction Condition- Time-90 min; Tempt.-90^0C; BC: Benzene- 1:6

4.2.5.Effect of Substrate

The effect of various substrates on the benzylation of benzene with benzyl chloride was investigated by keeping catalyst amount (0.200g), temperature (90^0C) and molar ratio of BC to substrate constant. Results are showed in the table 3. The benzene substrate showed monoalkylated product and others gives polyalkylated products depending upon the nature of the substrate. Anisole and toluene substrates gave faster reaction with 100% conversion compared to other substrates.

Table 3. Effect of substrate on benzylation of benzene with BC

Sr. No.	Substrate	Time (min)	% Conversion of BC	% Selectivity of DPM		
				Ortho	*Meta*	*Para*
1	Benzene	90	99.94	100	-	-
2	Toluene	80	100	45.33	-	54.67
3	Anisole	80	100	49.16	-	50.84
4	Bromobenzene	240	86.25	56.93	2.42	40.65
5	Chlorobenzene	90	98.39	38.76	1.56	59.68

Reaction Condition- Fe/CeO_2 (0.2g); Tempt.-90^0C; BC: Substrate- 1:6

4.2.6.Reusability

Finally reusability of the catalyst was investigated for benzylation of benzene with benzyl chloride over Fe/CeO_2 catalyst under the optimized reaction conditions showed in table 4. After the completion of the reaction, catalyst was separated from the reaction mixture, washed with acetone several times, dried and calcined at 500^0C for 2 hrs. The reaction was again performed on the reactivated catalyst. It was observed that using the catalyst for 4 cycles, its

activity decrease from 99.94 to 93%. After four reaction cycles catalyst was reused, it showed that catalyst may performed with significant loss of its catalytic activity. Upto four reaction cycles, it reveals that the catalyst was stable and reusable.

Table 4. Reusability of catalysts per cycles

Cycles	% Conversion of BC	% Selectivity of DPM
1	99.94	100
2	96.78	99.99
3	94.35	100
4	93.54	100

Reaction Condition- Fe/CeO_2 (0.2g); Time-90 min; Tempt.-90^0C; BC: Benzene- 1:6.

Among other catalyst Fe/CeO_2 exhibit good acid strength due to which conversion as well as selectivity increases. The catalytic activity was carried out with benzylation of benzene by using Fe/CeO_2 catalyst at temperature 90^0C, catalyst amount 0.2g with molar ratio 1:6 (BC:Benzene) gave higher % conversion of benzyl Chloride (99.94%) with 100% selectivity of Diphenylmethane as a product . Reuse of the catalyst for three times with similar results and recycling doesn't affect the efficiency of the catalyst.

CONCLUSION

Well-crystallized and dispersed nano-ceria and Fe(III), Co(II), Ni(II), and Cu(II) ceria catalysts were obtained by hydrothermal synthesis using an oxidizer H_2O_2. From XRD data concluded that all the prepared catalysts showed nanosized crystalline nature having crystallite size in range between 9-16 nm. The nano size of the catalysts was confirmed by good agreement between TEM and XRD analysis.

Friedal crafts benzylation of benzene was carried by using Fe/CeO_2 catalyst at temperature 90^0C, with molar ratio 1:6 (BC: Benzene) gave higher % conversion of benzyl chloride (99.94%) with 100 % selectivity of diphenylmethane as a product .

Reuse of the catalyst for three times with similar results and also proved that recycling does not affect the efficiency of the catalyst. Lewis acid sites of the catalysts are mainly responsible for the good catalytic performance in the benzylation reaction.

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