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Benzylation of aromatic compounds over environmentally benign antimony and bismuth supported zirconia catalysts

Manohar Basude*, Prasad Sunkara, Rajkumar Sheelam and Lingaiah Paka

Department of chemistry, Nizam College, Osmania University, Hyderabad

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ABSTRACT

The efficacy of the supported antimony, bismuth catalysts and unsupported antimony salt for catalyzing the benzylation reaction using benzyl chloride has been studied using microwave irradiation. The benzylation of aromatic compounds with benzyl chloride proceeded to afford diphenylmethane and its derivatives in high yields. The zirconia alone in the absence of antimony and bismuth oxides was little active. Comparing activities of zirconia, Sb/Bi supported zirconia and $SbCl_3$ as catalyst shows that supported zirconia catalysts gave higher conversion than their corresponding unsupported catalysts. XRD and IR results showed that the hydrous zirconia sample exhibited poor crystallinity with a mixture of monoclinic and tetragonal phases. On the other hand, the Sb, Bi promoted samples exhibit prominent lines due to tetragonal phase. Higher activity of supported zirconia catalyst is attributed to presence of greater amount of tetragonal phase of ZrO_2, redox potential and higher surface acidity.

Keywords: Benzylation; supported zirconia; tetragonal phase; microwave irradiation.

INTRODUCTION

Diphenylmethane is a valuable product in the chemical industry. The compound which is also known as benzyl benzene is used in organic syntheses, in dyes and in the perfume industry. In addition, the compound is also an intermediate which is used in the synthesis of benzophenone. The latter compound is also a valuable compound in the chemical industry, being used in organic syntheses, in perfumery, especially for floral odors, as a fixative, or as a ultra-violet sensitizer for photo polymerization, while derivatives of benzophenone are used as ultra-violet absorbers.

Friedel-Craft type reactions are considered as one of the most important reactions in organic synthesis. Benzylation of benzene using benzyl chloride to afford diphenylmethane is an interesting example. Homogeneous Lewis or Bronsted acid catalysts are used in Friedel-Craft type reactions (**1**). They create several problems such as polyalkylations and rearrangements which are difficult to avoid, in addition to corrosion, toxicity and catalyst recovery. An important step forward in overcoming these problems is the application of solid acid catalysts. A number of solid catalysts have been evaluated by Clark et al (**2**) and reported montimorillonite supported zinc (clay zinc) and Nickel Chloride are highly active for catalyzing Friedel-Crafts alkylation's. Zeolites are another class of catalysts which are extensively used in Friedel-Crafts alkylation reaction. V.R. Choudhary et al **(3)** has studied benzylation of benzene by benzyl chloride over Fe, Zn, Ga and In-modified ZSM-5 type catalysts and Ga, In-modified H-β type catalysts **(4),** higher activity for the Ga, In-modified Zeolites attributed to the redox properties of the catalysts. Fe-containing mesoporous molecular sieves are very active in benzylation of benzene and have better stability than the Fe-pillared clays. Temperature and pore size were two critical factors influencing the activities of the catalysts. A redox mechanism has explained the experimental results **(5).** Benzylation of benzene in liquid phase by benzyl chloride to diphenylmethane over $FeCl_3$, $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$ supported alumina has been investigated. The redox property of alumina supported transition metal chloride seems to play a important role in the benzene benzylation process. Among the catalyst, the $FeCl_3/Al_2O_3$ showed both high conversion and high selectivity for the benzylation of benzene **(6).** Sb supported K10 found to be very active even though the $SbCl_3$ is found to be least active lewis acid under homogeneous conditions **(7).** Such catalysts are interesting and efficient for organic synthesis because the catalyst is easily separated from the product and the organic reactions occur on the surface of alumina, and hence the reactivity and selectivity may be different from those in homogeneous solutions. Ga-, Al- and AlGa-SBA-15 mesoporous materials synthesized via a direct sol–gel hydrothermal protocol were found active and selective in the Friedel–Crafts alkylation's of toluene with benzyl chloride (promoted by Lewis acidity) and benzyl alcohol (promoted by Bronsted acidity). The solid acids were also highly reusable preserving almost their initial catalytic activity after five reuses **(8).** XRD and SEM results revealed that the amorphous and porous structure of RHA silica was retained after the incorporation of Al^{3+}, Ga^{3+} and Fe^{3+} ions. EDX analysis confirmed Al^{3+}, Ga^{3+} and Fe^{3+} ions were attached to the silica matrix and were homogeneously distributed.. The benzylation of benzene (Bz) and substituted benzenes with benzyl chloride (BC) were studied over the prepared catalysts. RHA–Fe showed excellent activity for the benzylation of benzene, whereas, RHA–Ga gave good selectivity towards diphenylmethane (DPM). Almost complete BC conversion and about 86% and 80% selectivity to DPM were obtained after 90 and 13 min over RHA–Ga and RHA–Fe, respectively. However, RHA–Al was found to be inactive under the reaction conditions studied. Catalytic activity of RHA–Ga with substituted benzenes showed a reverse trend to that of the conventional Friedel–Crafts reaction, i.e. benzene > toluene > ethyl benzene > anisole. The catalysts could be reused for the benzylation reaction several times without significant loss in their activity and selectivity **(9).** The catalytic activity of Ga-SBA-15 materials has been evaluated in the Friedel–Crafts acylation of anisole with benzoyl chloride and in the alkylation's of benzene using benzyl chloride as alkylating agent. The activity of these catalysts was compared with the one of Ga-modified SBA-15 by post-treatment. A complete conversion of benzyl chloride over Ga-SBA-15 materials has been reached after 3 h of reaction with 75 % selectivity toward diphenylmethane. In contrast to Ga-samples prepared by post-treatment, *in situ* Ga-SBA-15 present a lower stability in the acylation reaction. However, the catalytic results indicate that Ga-SBA-15 mesoporous materials can be used as versatile and stable acid catalysts for Friedel–Crafts reactions with appropriate behavior depending on their preparation mode **(10).** The performance of Fe-ZSM-5 catalysts (prepared by incipient wetness, 0.5–2.5% of Fe) for benzylation of benzene by benzyl chloride was studied and explained in terms of their chemical and adsorption properties. Reaction experiments, carried out in an isothermal batch reactor, showed that increasing amounts of iron lead to more active catalyst, but less selective for the formation of diphenylmethane. Results reported, suggest that the reaction is controlled by the adsorption and activation of the benzyl chloride. The addition of iron to the ZSM-5 zeolite largely increases the interaction between this compound and the catalyst surface (**11).** The benzylation of benzene and other aromatics by benzyl chloride to diphenylmethane over $FeCl_3$, $InCl_3$, $GaCl_3$, $ZnCl_2$, $CuCl_2$ and $NiCl_2$ supported on mesoporous SBA-15 at 353 K has been investigated. The redox property due to the impregnation of the SBA-15 by transition metal chloride seems to play a very important role in the benzene benzylation process. Among the catalysts, the $FeCl_3$/SBA-15 showed both high conversation and high selectivity for the benzylation of benzene. The activity of these catalysts for the benzylation of different aromatic compounds is in the following order: benzene > toluene > *p*-xylene > anisole **(12).** Dealuminated mordenite zeolite is used as solid acid catalyst in acylation of anisole by propionic anhydride. It was observed that after dealumination the pore size of the zeolite increases and facilitates the reactant to enter into it but there is no significant effect on acylation **(13).**

Innovative aspects are the development of new acid catalysts is within the frame work of the discovery of new solid acid catalyst to improve the yield and selectivity towards the target product. The synthetic method is easy providing zirconia with different degree of acidity depending on reaction requirement, which makes it potential catalyst for industry devoted to organic transformation. Zirconia based solid acid catalysts for catalyzing several reactions is described by Arata and Hino et al **(14).** Among solid super acid catalysts reported, sulfated zirconia received much attention due to its high activity to catalyze many reactions at low temperature **(15).** It is known that mixed oxides often show enhanced acidity and thermal stability than their constituent single oxides. Therefore we undertook investigations to prepare solid acid catalysts of Sb, Bi oxide doped zirconia

Microwaves on the other hand accelerate the chemical reactions in solvents as well as solvent free conditions and have witnessed explosive growth. Microwave irradiation often leads to shorter reaction time, increased yields and easier workup matching with green chemistry protocols. The availability of several publications in the literature clearly indicates the impact of microwave assisted reactions in organic synthesis **(16).** The aim of the present work is to promote the Friedel Craft benzylation reaction of aromatic compounds with benzyl chloride to diphenylmethane and its derivatives, using ZrO_2, Sb/ ZrO_2 and Bi/ ZrO_2 catalysts. The corresponding benzylated compound is obtained in high yields in microwave irradiation and solvent free condition.

EXPERIMENTAL SECTION

Preparation of the catalyst

Zirconia based solid acid catalysts were synthesized by precipitation and impregnation method using zirconia source. In the first step zirconium hydroxide was prepared by hydrolyzing salt $ZrOCl_2.8H_2O$ with aqueous ammonia solution. In preparation of zirconium hydroxide about 5 gm of $ZrOCl_2.8H_2O$ was dissolved in 40 ml of doubly distilled water. The p^H of the solution was 2. Dilute ammonia solution was added slowly until the p^H of the solution reached 7 with continuous stirring. The obtained precipitate was washed with distilled water several times until free from chloride ions and dried at 393K for 48 hrs. The oven dried sample was calcined at 873K to obtain ZrO_2.

In the second step impregnation of the Bi and Sb metal oxide promoter was carried out by dissolving requisite quantities of corresponding metal precursors $Bi(NO_3)_3$ $.5H_2O$ and $SbCl_3$ in doubly distilled water to which $Zr(OH)_2$ is added and the excess water is evaporated. In the preparation of 5% Bi_2O_3/ZrO_2 0.232 gm of $Bi(NO_3)_3$ $.5H_2O$ is taken in a beaker and dissolved in 20 ml water. To this solution about 2 gm of $Zr(OH)_2$ is added and water is evaporated on hot plate with continuous stirring. The obtained samples were oven dried at 393K for 48 hrs and finally calcined at 873K for 5h.

In the preparation of 5% Sb_2O_3/ZrO_2 0.9028 gm of $SbCl_3$ is dissolved in 20 ml of water. To this 4gm of $Zr(OH)_2$ is added and water is evaporated on hot plate with continuous stirring. The obtained samples were oven dried at 393K for 48 hrs and finally calcined at 873K for 5h.

Characterization

X-ray diffraction studies

The x-ray diffraction patterns of powder samples were recorded on X-ray diffractometer. The diffraction patterns of the samples are obtained using monochromatic CuK_α radiation of wavelength $\lambda = 1.54056\ A^0$. The X-ray tube operated at 15 mA/30 kV with 1000 W of x-ray power. The diffraction patterns were obtained in the range 10^0 to 70^0 in 2θ for all samples. From the powder XRD patterns of polycrystalline sample, the average crystallite size 'P' is determined by using the following Debey-Scherrer equation

$$P = K\ \lambda / \beta \cos \theta$$

Where
$K = 0 .89$
$\lambda = 1.54056\ A^0$
β = FWHM i. e., full width at half maxima

FTIR

Fourier transform infrared spectra of the samples were recorded on FTIR spectrometer at ambient conditions KBr was used as diluent.

Reaction procedure for benzylation of aromatic compounds

Microwave irradiation

A mixture of benzene (1m mol) and 20 mg of the catalyst was taken. To this benzyl chloride (1mmol) was added, homogenized and irradiated in a commercial microwave oven at 320 W. At the end of the irradiation, the mixture was cooled to room temperature and extracted with ether. The organic layer was dried over sodium sulphate and solvent was removed under vacuum. The product was subjected to silica gel column chromatography using 2% EtoAc in petroleum ether as eluent to get diphenylmethane and substituted diphenylmethane. After completion of the reaction isolated yields are determined quantitatively, qualitatively by NMR and compared with the authentic samples.

RESULTS AND DISCUSSION

Zirconia and Bi, Sb promoted zirconia catalysts are characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy. Particle size calculated using Debey-Scherrer equation of zirconia and Bi, Sb promoted zirconia catalysts varies between 10-30 nm. On addition of promoter there is increase in particle size.

Table 1 Crystallite size calculated using Debey-Scherrer equation for various catalysts

entry	catalyst	FWHM	2θ	Crystallite size (nm)	Average crystallite size (nm)
1	ZrO_2	.7449	30.47	11.55	10.26
		1.1267	50.63	8.154	
		.8667	60.38	11.09	
2	5% Bi/ZrO_2	.94	30.16	9.15	22.86
		.47	50.02	19.5	
		.24	59.84	39.92	
3	5% Sb/ZrO_2	.24	30.08	35.83	26.37
		.24	50.04	38.19	
		1.88	60.14	5.1	

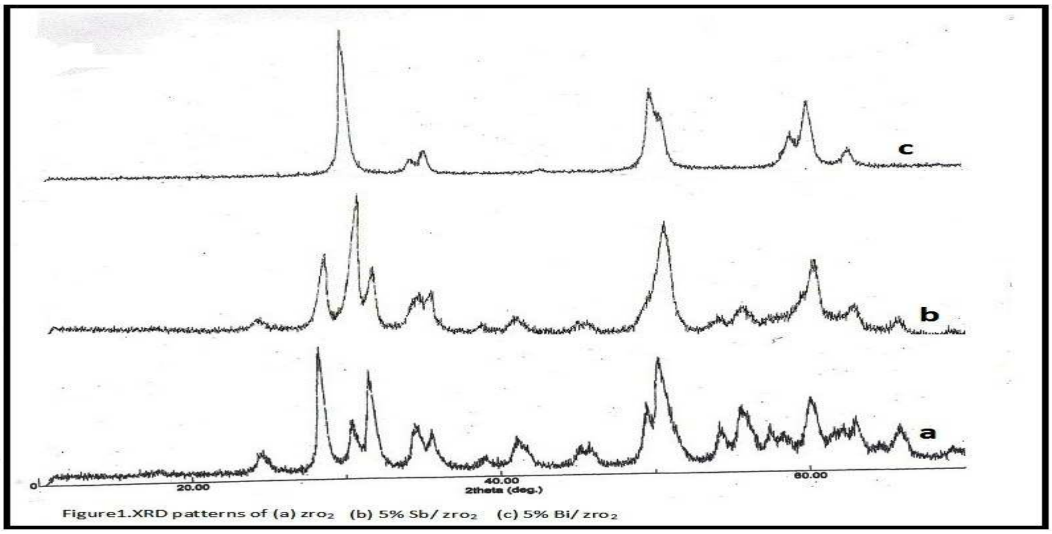


Figure 1. XRD patterns of (a) ZrO_2 (b) 5% Sb/ZrO_2 (c) 5% Bi/ZrO_2

The hydrous zirconia sample exhibited poor crystallinity with a mixture of monoclinic and tetragonal phases. On the other hand, the Sb, Bi promoted samples exhibit prominent lines due to tetragonal phase, indicating that the impregnated metal ions show a strong influence on the phase modification of zirconia from thermodynamically more stable monoclinic to the metastable tetragonal phase. Promoted zirconia shows larger crystallite size compared to the pure ZrO_2. XRD results in figure 1 confirm that incorporation of metal ions retard the formation of smaller crystallites of zirconia and stabilize them in the metastable tetragonal phase. Unpromoted ZrO_2 leads to the formation of thermodynamically more stable monoclinic form with smaller crystallites. In sample calcined at 500 ^{0}C, broad peaks of tetragonal phase are detected, indicating that the sample is in an intermediate amorphous to tetragonal form. The peaks of tetragonal phase become stronger when the sample is calcined at 600 ^{0}C as that of the peaks of the monoclinic phase. The peak intensities of the monoclinic phase grow steadily and those of the tetragonal phase decline with the increase in calcinations temperature to 700 ^{0}C and 800 ^{0}C. For the sample calcined at 800 ^{0}C, the monoclinic phase is predominant **(15).**

In figure 2 FTIR spectra of zirconia and promoted zirconia is shown. After cacination at 550 ^{0}C, the FTIR spectrum exhibits two shoulders close to 1067 and 937 cm$^{-1.}$are observed for zirconia close to reported values in literature. The 3400 cm^{-1} band intensity corresponding to stretching vibration of hydroxyl groups decreased strongly and better resolved bands are observed clearly close to 746, 557, 500 and 514 cm^{-1}, for bismuth promoted zirconia but not for antimony promoted zirconia which is characteristics of tetragonal form of crystalline zirconia. From this it is concluded that, because of calcination, condensation of hydroxyl groups of $Zr(OH)_2$ occurred, leading to a crystallized sample. Our results are very close to the reported values in the literature.

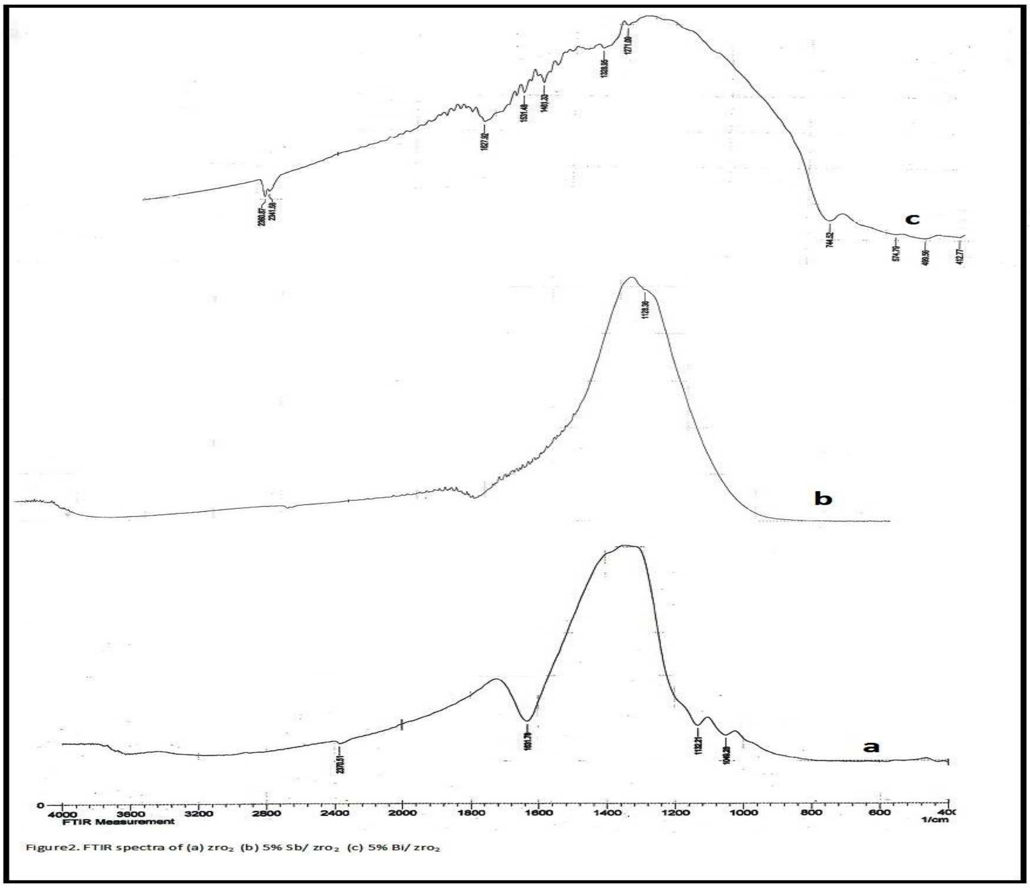


Figure 2. FTIR spectra of (a) ZrO_2 (b) 5% Sb/ZrO_2 (c) 5% Bi/ZrO_2

It was testified that the metal promoted zirconia calcined at 600 ^{0}C leads to formation of tetragonal phase and this catalyst is effective in catalyzing benzylation of the aromatic compounds in the present study. In benzylation reaction, the influence of the catalyst amount, material ratio and reaction time were studied. The optimum benzylation reaction conditions observed are: mole ratio of aromatic compound to benzyl chloride is 2: 1, weight of the catalyst used is 20 mg, time taken for completion of the reaction is as given in the table and reaction temperature is 80 ^{0}C - 100 ^{0}C at 320 W. With the increase in weight of the catalyst there was increase in conversion of benzyl chloride. With the increase in temperature there was increase in conversion and reaction was completed in shorter time. This solid acid can be reused several times in catalyzing the reaction.

The catalytic activities of various catalysts such as ZrO_2 and ZrO_2 supported antimony, bismuth catalysts are compared for their performance in benzylation of benzene at 320W(80 ^{0}C - 100 ^{0}C) in microwave assisted synthesis. From comparison of results (table 2) the following important observations can be made:

The zirconia support itself shows very little activity in benzylation of benzene; however its catalytic activity increased drastically because of impregnation of antimony and bismuth salts (tables 3-5). Among the supported antimony trioxide catalysts, the 5% Sb/ ZrO_2 showed both high conversion and selectivity in the benzylation. The conversion for the zirconia supported antimony trioxide catalyst is much higher than that for the $SbCl_3$ without any support.

The benzylation activity of the zirconia supported antimony and bismuth is in the following order in the case of substituted benzenes but in the case of benzene zirconia supported antimony is more active compared to zirconia supported bismuth.

5% Bi/ ZrO_2 > 5% Sb/ ZrO_2 > 3% Sb/ ZrO_2 > $SbCl_3$

Table 2.Benzylation of aromatic compounds using $SbCl_3$

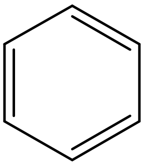
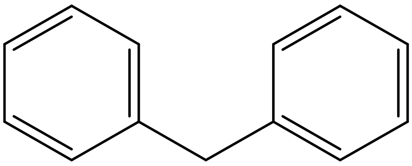
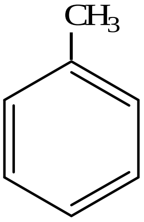
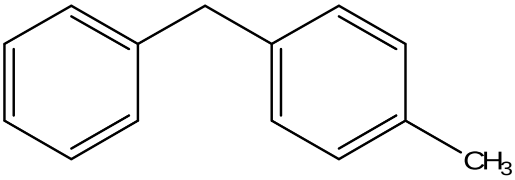
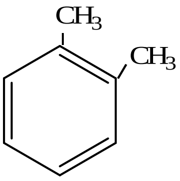
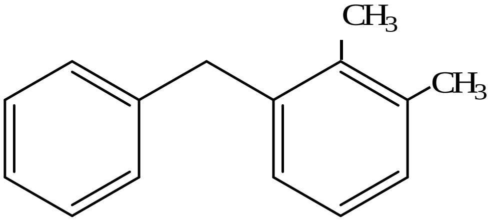
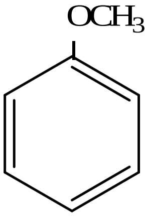
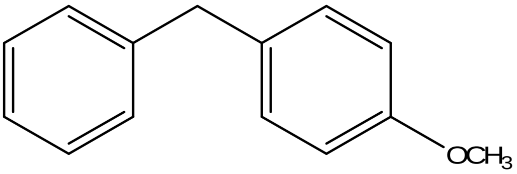
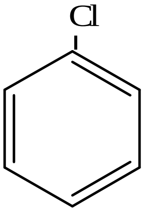
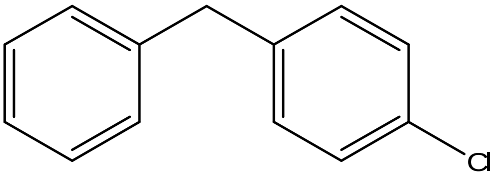
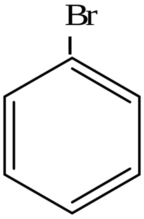
Entry	Reactant	Product	Time (min)	Yield%
1	 Benzene	 Diphenyl Methane	1	64
2			3	58
3			4	54
4			5	54
5			12	52
6		No reaction	_	_

Table 3 Benzylation of aromatic compounds using 3%Sb/ZrO_2

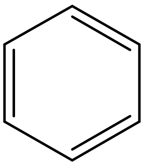
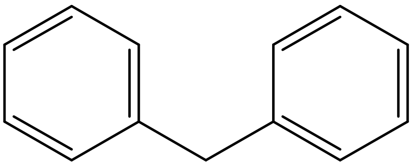
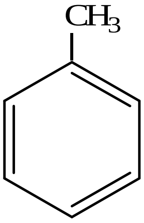
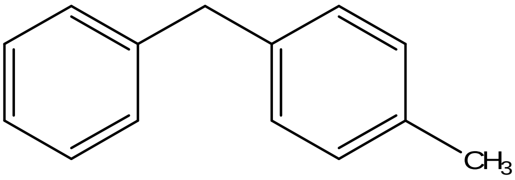
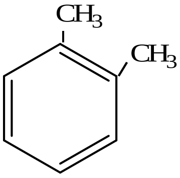
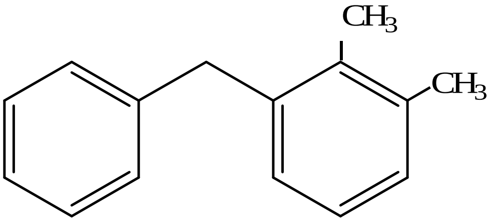
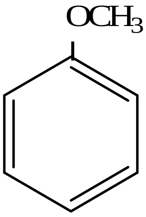
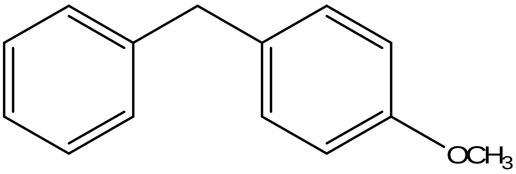
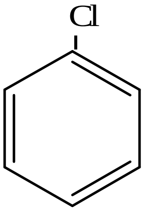
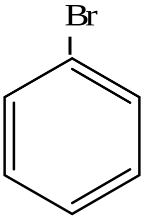
Entry	Reactant	Product	Time (min)	Yield%
1	 Benzene	 Diphenyl Methane	1	84
2			3	78
3			4	75
4			5	80
5		No reaction	-	-
6		No reaction	_	_

Table 4. Benzylation of aromatic compounds using 5% Sb/ZrO_2

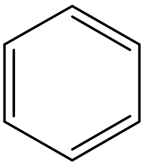
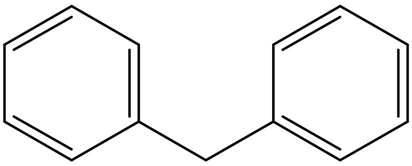
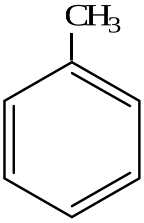
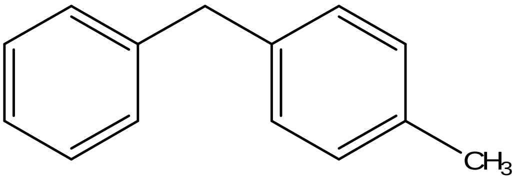
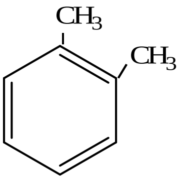
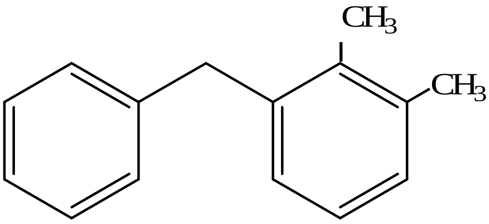
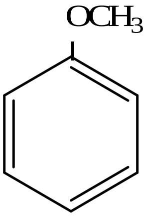
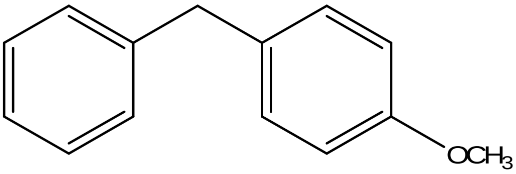
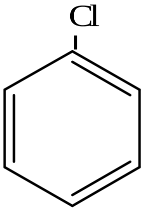
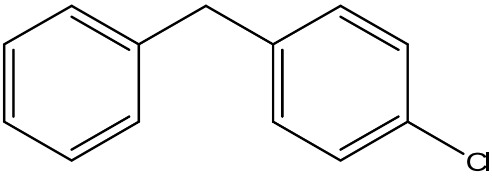
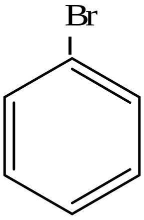
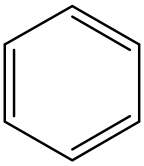
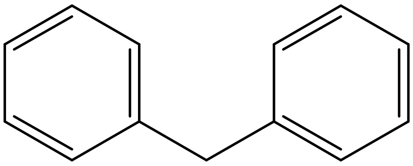
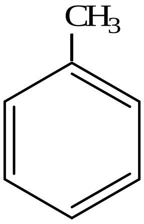
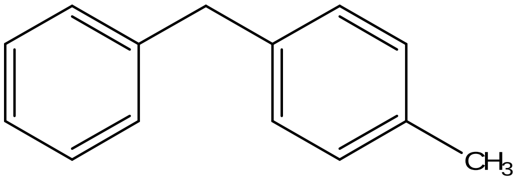
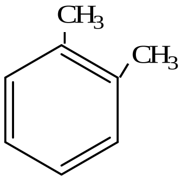
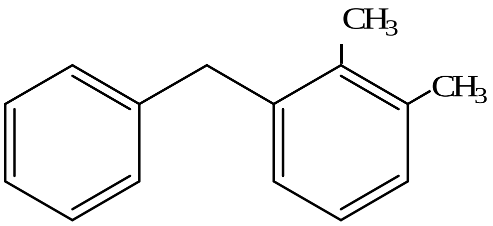
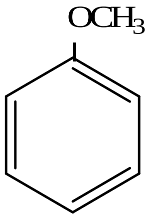
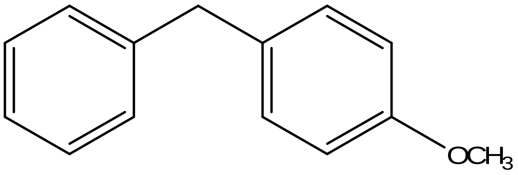
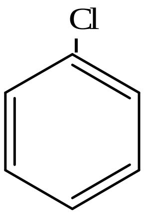
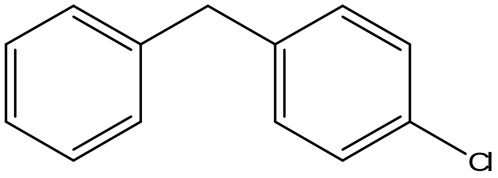
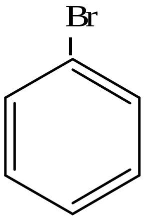
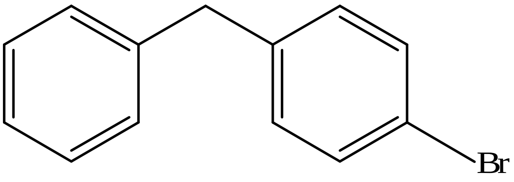
Entry	Reactant	Product	Time (min)	Yield%
1	 Benzene	 Diphenyl Methane	1	90
2			3	82
3			4	80
4			5	84
5			12	68
6		No reaction	–	–

Table 5. Benzylation of aromatic compounds using 5% Bi/ZrO_2

Entry	Reactant	Product	Time (sec)	Yield%
1	 Benzene	 Diphenyl Methane	240	92
2			40	85
3			80	80
4			110	86
5			70	75
6			300	60

It is interesting to note that higher activity of bismuth over antimony supported zirconia catalyst in benzylation of substituted benzene is quiet similar to that of the redox potential of the metal in the supported metal oxide catalysts. This indicates a close relationship between the redox potential and the catalytic activity of the supported metal oxide catalysts.

Higher activity of the supported 5% Sb/ ZrO_2 over $SbCl_3$ is attributed to increase in exposed area of the active component on the support, higher surface acidity due to formation of the tetragonal phase and higher redox potential. At the end of the reaction, the catalyst was separated by filtration, thoroughly washed with the solvent and reused under similar conditions. These catalysts can be reused for the benzylation several times. However they showed slightly lower activity. This clearly indicates strong binding of the active component on the support. However, there is appreciable loss in activity when active component is anchored on support using some organic solvent. This is expected mostly because of the leaching of the active catalyst component during the benzylation reaction.

As can be seen from the tables, the rate of benzylation was dependent on the nature of the aromatic compound employed. We first examined the reaction between benzene and benzyl chloride at 320 W. The reaction was very fast and completed in one minute. Benzene was more reactive than the substituted benzenes over antimony based catalysts and in the case of bismuth supported catalysts. Bromobenzene which is inactive over antimony based catalysts shows reasonable activity over bismuth promoted zirconia catalyst.

Effect of catalyst concentration

The reaction profile using different amount of catalyst revealed that selectivity to diphenylmethane was higher at a lower concentration. At the higher concentration of the catalyst the conversion of benzene increased to an optimum value and formation polymerized product also increased simultaneously. Hence an optimum of 20 mg of the catalyst in the reaction mixture was ideal for achieving better conversion and selectivity for diphenylmethane in microwave assisted benzylation of benzene and substituted benzenes 320W.

Effect of temperature

Reactions were carried out using the catalyst in the temperature range of 50-120 ^{0}C(160 W - 320W). It was found that conversion were very poor at lower temperature of 50 ^{0}C (160 W). A temperature of at least 80 ^{0}C is required for appreciable conversion and (diphenylmethane) selectivity to product. On increasing the temperature from 80 ^{0}C to 120 ^{0}C (>320 W), the formation of diphenylmethane decreased as expected. High reaction temperature favors the formation of polymerized product.

Effect of benzene/benzyl chloride molar ratio

The selectivity towards diphenylmethane over catalysts can be improved at higher dilutions of the benzyl chlorides. At higher molar ratio of 5:1benzene/benzyl chloride higher selectivity to diphenylmethane is achieved. However, such a high molar ratio of benzene/benzyl chloride is impractical for industrial use, since unreacted benzene has to be recovered and recycled. A more reasonable molar ratio of benzene/benzyl chloride is 2:1for greater selectivity to desired product.

CONCLUSION

The benzylation of benzene/substituted benzenes with benzyl chloride using zirconia supported and unsupported catalysts have been investigated. Comparing activities of zirconia, Sb, Bi supported zirconia and $SbCl_3$ as catalyst shows that zirconia supported catalysts gave higher conversion than their corresponding unsupported catalysts. The following conclusions may be drawn:

The major product of benzylation of benzene(substituted benzene) with benzyl chloride is diphenylmethane(substituted diphenylmethane)

The Bi_2O_3/ZrO_2 is highly active catalyst for the benzylation of substituted benzene with benzyl chloride.

The zirconia supported catalyst did not undergo any color change during the reaction and could be easily separated and can be reused many times.

The zirconia alone in the absence of antimony and bismuth oxides was little catalytically active. The activity of substituted benzene benzylation decreases in the following order 5% Bi/ ZrO_2 > 5% Sb/ ZrO_2 > 3% Sb/ ZrO_2 > $SbCl_3$.

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