Liquid phase mononitration of chlorobenzene over WO_x/ZrO_2: A study of catalyst and reaction parameters

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Abstract

To study the effect of W concentration and activation temperature of the catalysts a series of WO_x/ZrO_2 samples with varying concentration of W (10–25 wt.%) were prepared and activated at 650/750 °C. XRD of sample shows 15 wt.% W stabilizes the tetragonal phase of zirconia up to 750 °C. Above and less than 15 wt.% shows peaks corresponding to monoclinic WO_3 and monoclinic ZrO_2, respectively. Further, the tungsten modification stabilizes the specific surface area of ZrO_2. There is an increase in the surface area observed up to 15 wt.% W, which declines on further increase in the concentration. The NH_3 TPD confirms the presence of acid sites with varying strength from the broad desorption profile. The 15 wt.% W and activated at 750 °C shows maximum acidity. The results of the nitration reaction of chlorobezene imply the 15 wt.% W and activation at 750 °C shows maximum activity. Not only yield, a better *para*-selectivity is also achieved with WO_x/ZrO_2 samples. Effect of activation temperature, W concentration and reaction parameters such as reaction temperature, reaction time, the presence of solvent and solvent free medium on activity and selectivity are studied in details.
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1. Introduction

Nitration of aromatic compounds is a ubiquitous reaction to realise organic intermediates required in large tonnages for the fine chemical industry. Mononitrohalobenzene, especially *para*-nitrochlorobenzene, are versatile intermediates for dyes, pharmaceuticals and perfumes [1]. The conventional nitration process [2,3], employing a nitrating mixture of nitric and sulfuric acid, for the last 150 years has remained unchallenged in the commercial arena owing to uneconomical alternative options. By classical method with a mixture of nitric and sulphuric acids, predominantly *ortho*- and *para*-products close to the ratio of 1:2 are resulted [2,3]. Due to the commercial importance of *para*-chloronitro benzene, a lot of studies were carried out to increase the *para*-selectivity. A mixture of acetic anhydride and nitric acid in the presence of sulphuric acid was used by Menke [4] and Paul [5] and afforded high *para*-selectivity at low temperature.

Although the conventional method of using concentrated H_2SO_4 provides better yield and selectivity too, the main disadvantage of this process is handling of the corrosive acid and also the waste acid disposal causes serious environment threats. In addition, the separation of products is another difficult step in this process. As in the recent time more emphasis has been given to develop clean process, it is essential to find a suitable alternate catalyst to meet the requirements. Use of solid acid catalyst seems to be the right solution.

In this contest, it was reported that claycop can produce 98% yield having ortho to para ratio of 13:85 when fuming nitric acid is used as the nitrating agent [6]. Choudhary et al. [7] claimed to increase the ortho to para ratio to 8:92 using Fe^{3+} exchanged montomorillonite-K10 catalyst in presence of nitric acid and acetic anhydride. Also, pillared clay was studied for this reaction as a solid acid catalyst [8]. Even beta-zeolite was used as catalyst for the same reaction [9] and reported to be efficient. Similarly several other reports are also available in the recent past in studying the nitration reaction of aromatics using solid acid catalysts [10–15].

The application of SO_4^{2-}/ZrO_2 catalyst in the nitration reaction of halobenzenes is reported first time by us [16]. It has

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been found that $SO_4{}^{2-}/ZrO_2$ gives better yield and also provide high *para*-selective in nature. Like sulphate modified zirconia, tungstate modified zirconia has been seen to be the key attraction of several researchers. Since it was first reported by Hino and Arata [17], it has been seen to be used in many catalytic reactions particularly for isomerisation of C_4–C_8 alkanes and alkylation of hydrocarbons [17–21]. Although WZ is much less active than sulphated zirconia it offers an important advantage as the WO_x in WZ are much more stable than the sulphate groups in sulphated zirconia at high temperatures [22] and in reductive atmospheres [23]. Besides these isomerisation reactions, WO_x/ZrO_2 catalysts also, find applications for acetylation of alcohols and phenols [24,25], liquid-phase alkylation of phenol with long-chain olefins [26], oxidation of ethylene to acetic acid [27].

Recently it has been attempted to use the WO_x/ZrO_2 catalyst for the nitration reaction. Brei et al. [28] has reported the vapour phase nitration of benzene using this catalyst. However, there are many issues like the catalyst preparation, activation and the reaction conditions such as effect of temperature, with and without solvent, reaction time, etc. are need to be addressed in details.

Santiesteban et al. [20] has shown that co-precipitation method involving the simultaneous precipitation of tungsten with the formation of the hydrous zirconia yielded a catalyst with higher strong acid sites compared to impregnation method. Therefore, in the present study, we have carried out the reaction using WO_x/ZrO_2 catalysts prepared by co-precipitation method with varying concentration of W and activated at different temperatures. Further, the effect of various reaction parameters on activity and selectivity of the catalysts are also studied.

2. Experimental

2.1. Sample preparation

A series of WO_x/ZrO_2 samples with varying concentration of tungstate was prepared following the co-precipitation method [20] and for comparison a sample without tungstate was also prepared.

The activation of the catalysts were done in an air Muffle furnace maintained at desired temperature of 650 and 750 °C with a heating rate of 3 °C/min and the catalysts were calcined for 3 h continuously and then allowed to cool naturally up to 110 °C. The catalysts were then cooled further to room temperature under desiccation for further studies.

2.2. Chemical analysis

The tungsten content was determined spectrophotometrically by the thiocyanate method at $\lambda = 400$ nm [29,30]. A weighed amount of sample was fused with $KHSO_4$ and then dissolved in water to 50 ml. About 15 ml concentrated HCl, 5 ml of $SnCl_2$ (45 g of $SnCl_2$ dissolved in 50 ml of concentrated HCl + 50 ml water), 2 ml of $TiCl_3$ freshly prepared (5 ml of $TiCl_3$ 15% diluted to 50 ml) and 10 ml aliquot of NH_4CNS solution (3 M) were then

added to a 10 ml aliquot of the tungsten-containing solution in a 50 ml volumetric flask. The solution was diluted to a mark and set aside for 30 min to ensure that the reaction of reduced tungsten (by $SnCl_2 + TiCl_3$) with thiocyanate ions induced full colour development. The absorbance of the test samples were recorded using a UV–vis spectrophotometer (Varian, Cary-1E, Australia) at preset wavelength of 400 nm. The standard solution was prepared by dissolving ammonium meta tungstate. The calibration curve, in the range 2–12 ppm, was obtained from standard solution of W(VI).

2.3. Characterisation

The powder X-ray diffraction of the WO_x/ZrO_2 samples was recorded with the help of a Philips (Model 1710) semi automatic X-ray diffractometer. It has auto divergent slit and graphite monochromator. The Cu Kα radiation was used with a scanning speed of 2°/min.

Surface area (BET), pore volume, average pore radius and pore size distribution of the WO_x/ZrO_2 samples were determined by nitrogen adsorption–desorption method at liquid nitrogen temperature (77 K) using a Quantasorb, supplied by Quanta Chrome, USA.

The temperature programmed desorption (TPD) of WO_x/ZrO_2 samples were carried out on a TPD/TPR/TPO (SIGMA, India) micro pulse reactor. For these experiments 0.2 g of the catalysts was accurately weighed and plugged at the center of a stainless steel micro reactor by the help of glass wool. The catalysts were pre-heated in oxygen flow at 550 °C for 3 h followed by nitrogen for a period of 1 h. The ammonia was then adsorbed on to the catalyst surface by carrying it by adapting a suitable technique-bubbling nitrogen in 25% ammonia solution and then through a cold trap to arrest the moisture if any carried along with ammonia. The ammonia adsorption continued at 100 °C till it is completely saturated and then desorbed for few more time at this temperature in order to remove physisorbed ammonia. Then after, the NH_3 desorbed starting from 100 to 600 °C in continuous flow of nitrogen (30 ml min^{-1}) at a heating rate of 10 °C/min is monitored. The amount of ammonia desorbed was monitored with the help of an on-line gas chromatography equipped with a thermal conductivity detector (TCD) and porapak-'N' packed column.

2.4. Catalytic activity

The nitration of chlorobenzene (CDH, AR) was carried out in a flask having provision of water circulation in order to maintain the reaction temperature. A magnetic stirrer was employed for constant stirring of the reaction mixture.

For each set of reaction, 10 mmol chlorobenzene and an equivalent quantity of nitric acid and acetic anhydride were used. The amount of acetic anhydride was chosen such as to be minimum that would allow quantitative conversion to acetyl nitrate. Accurately weighed 0.5 g of the catalyst was used in each case except for the blank experiment. For reaction carried out in presence of solvent, 10 ml of CCl_4 was used in each case. These quantities are kept constant irrespective of reaction tempera-

tures, reaction time (duration) and whether in solvent or solvent free medium. In the study of sequential addition of reagents, the reagents were added in various ways. However, the results presented in this work correspond to the optimum condition that is where the catalyst was being added after the addition of acetic anhydride and nitric acid.

The addition of nitric acid followed by acetic anhydride is always carried out very slowly keeping the reaction flask over a crushed ice bath in order to absorb the heat produced because of endothermic nature of the reaction (formation of acetyl nitrate).

After addition of all the ingredients, the whole reaction mixture was stirred with the help of a magnetic stirrer and the flask fitted with a condenser. The reaction temperature was maintained at RT (28 °C)/50 °C/70 °C by circulating heated water around the flask. After the end for every set of reaction, the reaction mixture was allowed to cool down to room temperature. The content was filtered using a Whattman filter paper no. 40. Acetic acid which is the only by-product and CCl_4 were separated by distillation. The percentage of *ortho-* and *para*-isomer of the nitrated product were analysed by gas chromatography (GC 17A Shimazdu, Japan) using 15% FFAP on 80/100 mesh W (HP) packed column and a flame ionization detector. In order to calculate the percentage *ortho-* and *para*-isomer, standard compound of nitro chlorobenzene was used.

3. Results and discussions

3.1. Chemical analysis

The weight percentage of W in different samples is shown in Table 1. The table shows the W wt.% as calculated during preparation and it also include the value measure by spectrophotometrically at $\lambda = 400$ nm (by the thiocyanate method) after it is being synthesized. It can be seen from table that the difference between the calculated and chemical analysis result of W concentration in different samples are very negligible. This indicates the complete co-precipitation and also proper dispersion of W in samples. For indicating a sample with a certain W concentration is however followed as was synthesized.

3.2. Charaterisation

Figs. 1 and 2 represent the XRD patterns of WO_x/ZrO_2 samples activated at 650 and 750 °C, respectively. It can be seen that the unpromoted zirconia activated at 650 °C shows peaks corresponding to monoclinic phase of zirconia with a minor amount
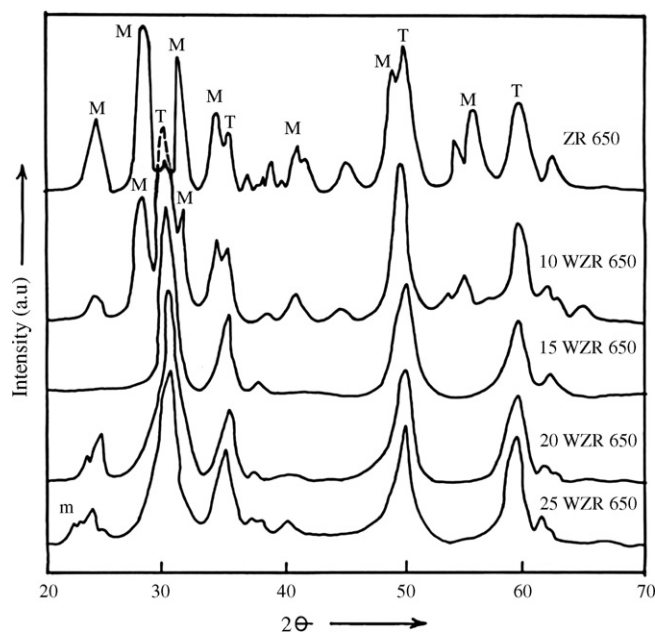
Table 1
Elemental analysis of WO_x/ZrO_2 samples

Sample details	'W' as calculated during synthesis (wt.%)	'W' as calculated by chemical analysis (wt.%)[a]
10WZR	10.0	9.89
15WZR	15.0	14.94
20WZR	20.0	19.88
25WZR	25.0	24.97

[a] 110 °C heated samples.

Fig. 1. XRD of WO_x/ZrO_2 samples activated at 650 °C. M, monoclinic-ZrO_2; T, tetragonal-ZrO_2; m, monoclinic-WO_3.

of tetragonal zirconia. However, from the XRD patterns of the WO_x/ZrO_2 samples it is noticed that the tungsten modification on zirconia influenced its crystallization. From the peak intensities it is observed that WO_x modification stabilizes the tetragonal phase. It can be seen that the WO_x/ZrO_2 sample with W concentration of 10 wt.% and activated at 650 °C contains peaks corresponding to tetragonal phase along with a minor amount of monoclinic zirconia. But if we see the pattern of 15 wt.% W sample it is interesting to note that peaks corresponding to mon-
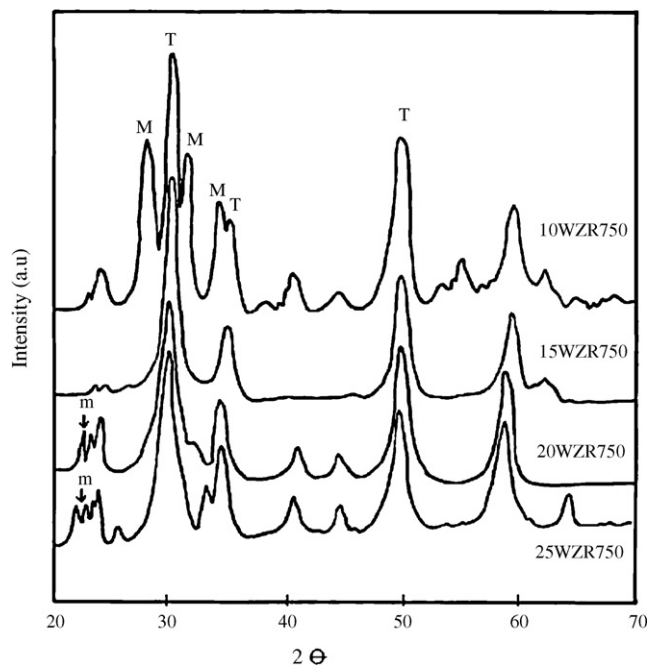

Fig. 2. XRD of WO_x/ZrO_2 samples activated at 750 °C. M, monoclinic-ZrO_2; T, tetragonal-ZrO_2; m, monoclinic-WO_3.

oclinic phase has totally eliminated and peaks corresponding to tetragonal phase are only found. This indicates the tetragonal phase stabilization effect of tungsten modification on zirconia. Although, 1% crystalline WO_3 can be detected by XRD, in the present case up to 15 wt.% W no peak corresponding to crystalline WO_3 is observed. This observation indicates the thorough dispersion of tungsten species throughout zirconia by the method of synthesis adapted (co-precipitation) and therefore presumably it could not crystallize separately. However, the sample containing 20 wt.% W shows the very minor presence of monoclinic WO_3 indicated from its characteristic peaks. When the concentration further increased to 25 wt.% W the peaks corresponding to monoclinic WO_3 are more prominently visible.

The 20 wt.% W sample which had shown only a minor presence of monoclinic WO_3 when activated at 650 °C shows more prominent and intense peaks corresponding to the presence of monoclinic WO_3 when calcined at 750 °C. In case of 25 wt.% W loaded sample it has also found to crystallize the monoclinic WO_3. However, it can be seen that XRD pattern of 15 wt.% W loaded sample did not show any peaks corresponding to the presence of monoclinic WO_3 even at activation temperature of 750 °C.

The above results suggest that the WO_x/ZrO_2 samples prepared by co-precipitation method followed by digestion are influenced by the presence of tungsten species in stabilizing the tetragonal phase. The 15 wt.% W is found to be 100% tetragonal phase zirconia up to activation at 750 °C. Whereas concentration above 15 wt.% W shows the presence of monoclinic WO_3 and below it shows the presence of monoclinic zirconia. Our results are similar to the inference noticed on other reports. From the literature it has been seen that the preparation procedure, concentration of W and activation temperature does affect the crystallization of zirconia and WO_3 separately [31–33].

Table 2 collects the BET surface area and average pore diameter of WO_x/ZrO_2 samples. It can be seen that zirconia sample prepared by similar method except modification by tungsten shows a specific surface area of 71 m^2/g when activated to 650 °C and which further decreases with increase in the activation temperature to 750 °C. We can see from the table that there is no much difference in surface area of different WO_x/ZrO_2 samples calcined at 110 °C rather it can be said that with increase in the W wt.% in samples there is decrease in the surface area. However, it is very interesting to note that on activation of the samples at 650

and 750 °C the tungsten modified samples retains higher surface area compared to the unpromoted zirconia sample. This confirms the surface area stabilizing effect of tungsten modification on zirconia. It is further noticed that with increase in the concentration of W in the samples up to 15 wt.% an increase in the specific surface area is observed which start decrease on further increase in the W loading. The decrease in the surface area with increase in W concentration beyond 15 wt.% can be correlated with the XRD results. The presence of monoclinic WO_3 as indicated from the XRD pattern could be the reason for the decrease in the surface area at higher concentration. The crystallization of WO_3 must have resulted in sintering of particles and hence decrease in the surface area. This particular argument is based on earlier results [34], which has predicted the strong interaction of WO_x species with ZrO_2 crystallites helps in inhibiting sintering. Also, Sarish et al. [26] has recently reported similar observation of the role of W as an effective inhibitor for sintering.

The decrease in surface area with increasing in activation temperature is as expected but it has been seen that tungsten modification stabilizes the surface area to a great extent. While the sample not promoted with tungsten shows a surface area of 32 m^2/g at 750 °C the sample promoted with tungsten (15 wt.%) is seen to retain surface area of 133 m^2/g for activation at same temperature.

The BJH mean pore diameters of WO_x/ZrO_2 samples are included in Table 2. It can be seen that as the calcination temperature of the samples increase there is a steady increase in the average pore diameter. In case of unpromoted zirconia it is little wider compared to the W promoted samples. Unlike surface area, the average pore diameter of the samples do not vary much with varying in the tungsten loading of the samples.

The surface acid sites measurements of the WO_x/ZrO_2 samples carried out by ammonia TPD are presented in Fig. 3. It can be seen that the TPD profile of ammonia shows a broad band (ammonia desorption) starting from 200 to 600 °C. The area under the curve represents the total acid site distribution. While the peaks on the ammonia desorption profile indicates the strength of acid sites. From the desorption profiles of various samples it can be easily said that sample with 15 wt.% W possesses comparably higher acidity than other samples. Similarly comparing the curves, it can also be pointed out that samples activated at 750 °C are more acidic compared to the same samples activated at 650 °C. However, this particular observation

Table 2
Specific surface area, average pore diameter (BJH) of WO_x/ZrO_2 samples

Sample	Surface area (m^2/g)[a]	Average pore diameter (Å)	Surface area (m^2/g)[b]	Average pore diameter (Å)	Surface area (m^2/g)[c]	Average pore diameter (Å)
10WZR	382	35.7	112	43.1	103	63.5
15WZR	378	36.4	138	48.5	133	62.1
20WZR	364	37.8	136	50.2	129	65.4
25WZR	358	40.7	114	46.8	104	70.1
ZR	381	58.9	71	70.2	32	80.4

[a] Samples calcined at 110 °C.

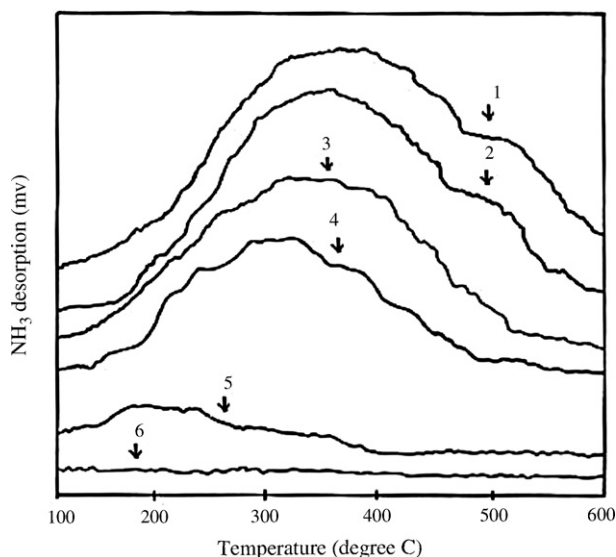[b] Samples activated at 650 °C.

[c] Samples activated at 750 °C.

Fig. 3. NH$_3$ TPD of WO$_x$/ZrO$_2$ samples. [Profile: (1) 15WZR750; (2) 20WZR750; (3) 15WZR650; (4) 10WZR650; (5) ZR650; (6) blank run.]
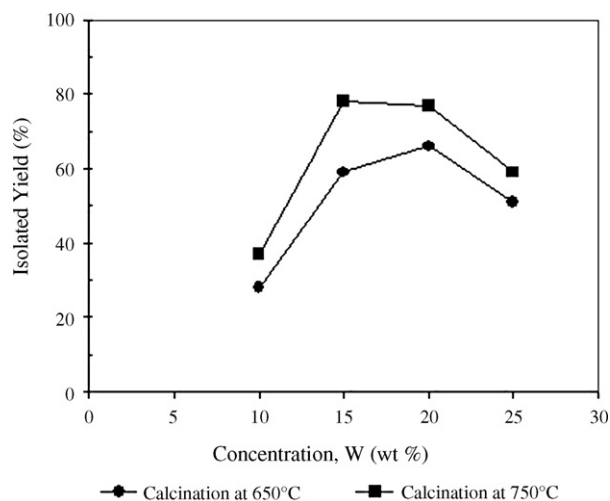

Fig. 4. Effect of W loading concentration on percentage yield. Catalyst: 0.5 g, 10 mmol chlorobenzene and equivalent quantities of acetic anhydride and nitric acid; time: 60 min and at room temperature.

is noticed for samples only up to 20 wt.% W and beyond this concentration, with increase in the activation temperature from 650 to 750 °C the TPD profile indicates a decrease in the number acid sites and as well as in their strength. The above results of ammonia TPD can be correlated with the XRD and surface area results. The appearance of peaks corresponding to monoclinic WO$_3$ for WO$_x$/ZrO$_2$ samples with concentration more than 20 wt.% W and activation at 750 °C which further prominent the presence of WO$_3$ could be the reason for less surface acid sites. The surface areas of the samples are also noticed to follow similar trend.

3.3. Catalytic activity

Table 3 collects the reaction and product details of the mononitration of chlorobenzene using WO$_x$/ZrO$_2$ catalysts. It can be seen that with increase in the tungsten (W) loading of the 750 °C calcined samples from 10 to 15 wt.%, there is an increase in the

Table 3
WO$_x$/ZrO$_2$ catalysed nitration reaction of chlorobenzene in solvent free medium

Catalyst	Reaction temperature	Reaction time	% Yield	*para*: *ortho*
10WZR650	RT	60	28	86:14
15WZR650	RT	60	59	83:17
20WZR650	RT	60	66	81:13
25WZR650	RT	60	51	85:15
10WZR750	RT	60	37	88:12
15WZR750	RT	60	78	86:14
20WZR750	RT	60	77	82:18
25WZR750	RT	60	63	84:16
15WZR750 (reused)	RT	60	75	85:15
20WZR750 (reused)	RT	60	73	83:17
Blank	RT	60	3	70:30

Reaction conditions: 10 mmol chlorobenzene and equivalent quantities of acetic anhydride and nitric acid, catalyst: 0.5 g.

catalytic activity and with further increase up to 20 wt.% of W, the activity remains almost constant. From the plot of W loading concentration versus percentage yield (Fig. 4) a plateau is clearly seen for W concentration in the range between 15 and 20 wt.%. Concentration above 20 wt.% in the sample results in decline of its catalytic activity. However, with varying in the concentration of W loading of the samples, it hardly affects the selectivity to the different isomeric products i.e., *para* and *ortho*. This clearly indicates that with increase in the W loading of the sample up to 15–20 wt.% W generates maximum number of Brønsted acidic site capable of nitration reaction and has also, Lewis acidic sites contributing towards *para*-selectivity of the catalysts.

3.3.1. Effect of catalyst activation temperature

It can be seen from Table 3 that all the WO$_x$/ZrO$_2$ samples in the concentration range of 10–25 wt.%, activated at 750 °C are found to be more active compared to the samples activated at 650 °C. It can be clearly observed from the plot of W concentration versus activity of samples (Fig. 4) that the activity curve for 750 °C is always above the curve obtained for 650 °C activated samples. Again, it can be seen that the catalytic activity trend of 750 °C activated samples follows the same as that of 650 °C activated samples (with varying the concentration of W loading). However, it is observed that among the 15 and 20 wt.% W loaded samples, activation at 650 °C results in a wide variation in their activities for the nitration reaction while samples activated at 750 °C are found very close in their activities.

This implies, activation at 750 °C creates more numbers of strong acid sites capable of nitration reaction and 15–20 wt.% of W must be optimum to give a mono layer coverage of the W (WO$_x$) species resulting in creation of more number of Brønsted acid sites. From the above results, it can be said that 15 wt.% W is just enough to produce mono layer coverage and 20 wt.% is bit higher than required and probably that could be the reason of less activity of the sample when calcined at 650 °C. However, calcinations at higher temperature, i.e., 750 °C made the catalyst

more active though the formation of WO$_3$ species is observed from XRD peaks.

The decline in activity with further increase in concentration beyond 20 wt.% W could be presumably due to the formation of relatively higher amount of tungsten oxide species resulting overall decrease in the acidic sites of the catalyst. The WO$_3$ is non-acidic in nature and hence not capable of nitration reaction. In addition, it has been explained that the formation of WO$_x$ also blocks the pores and therefore hinders the approach of the reacting molecules to the active sites. The above justification is well supported with the XRD pattern of the samples, the peaks indicates the presence of WO$_x$ species in samples with W loading of 20 wt.% and more. Though the appearance of the m-WO$_x$ are not very prominent for sample with 20 wt.% it is quite clear for the sample with 25 wt.% W. Like the decline in activity of the catalysts with variation in the W concentration, there is no effect on selectivity of the products. This indicates activation of WO$_x$/ZrO$_2$ at 750 °C creates more numbers of strong acidic sites capable of nitration reaction.

The mechanism/scheme we have proposed for the nitration of halobenzenes using SO$_4^{2-}$/ZrO$_2$ as catalyst [16] explains how the presence of Brønsted and Lewis acid sites over SO$_4^{2-}$/ZrO$_2$ controls the activity and selectivity as well. The Brønsted acid sites facilitate the formation of NO$_2^+$ and hence the nitration while the Lewis acidic sites facilitate the attack of NO$_2^+$ ion at *para*-position and therefore results improved *para*-selectivity of the catalyst.

Hence, activity more than 78% and selectivity about 85% achieved using WO$_x$/ZrO$_2$ as catalyst in the nitration reaction of chlorobenzene at room temperature confirms the presence of strong Brønsted and Lewis acid sites over surface of the catalyst. The catalysts on reuse are found to be active with a very little decrease in their activity. The values are presented in Table 3.

When a blank experiment was carried out without using any catalyst but keeping all other reaction conditions similar, a very low yield was obtained that is 3%. The yield without any catalyst could be due to the excess protons of the nitric acid on reacting with acetyl nitrate helps in production of NO$_2^+$ ions and hence the nitration reaction. However, the selectivity in this case obtained is only 70:30 (*para*: *ortho*).

3.3.2. Effect of reaction temperature on activity and selectivity of WO$_x$/ZrO$_2$ (with and without solvent)

Experiments have shown that the reaction without any solvent exhibits more yield compared to that of reaction conducted using CCl$_4$ as solvent. The reaction temperature has also seen to affect the final yield. In the present study, reactions conducted between room temperature (RT) to 70 °C are presented in Table 4. It can be seen that reaction conducted at 50 °C yields maximum, however, reaction at RT (28 °C) also fetches a fairly good yield that is only slightly less than the yield obtained when the reaction was carried out at 50 °C. The yield (78%) obtained at 70 °C without solvent is less than the yield (72%) in the presence of solvent. At higher reaction temperature the acetyl nitrate, which is responsible to bring the nitration of the chlorobenzene, must be undergoing decomposition and is not available for reaction. However, when the reaction was carried out at same reaction

Table 4
Effect of reaction temperature on yield and selectivity (with and without solvent)

Reaction temperature (°C)	Reaction without solvent		Reaction with CCl$_4$ as solvent	
	Yield (%)	*para*: *ortho* (%)	Yield (%)	*para*: *ortho* (%)
∼0	21	82:18	–	–
28	78	86:14	68	86:14
50	83	86:14	81	87:13
70	72	85:15	77	83:17

Reaction conditions: 10 mmol chlorobenzene and equivalent quantities of acetic anhydride and nitric acid; catalyst (15WZR750): 0.5 g; reaction time: 60 min, 10 ml CCl$_4$.

temperature (70 °C) but in the presence of CCl$_4$ as solvent yields more compared to reaction at RT and without any solvent. This indicates that in presence of solvent the decomposition of acetyl nitrate is presumed to be less and hence result in more yields. However, from the tables, it can be seen that when the reaction is carried out at 50 °C it yields maximum irrespective of solvent free or in presence of solvent.

3.3.3. Effect of reaction time on nitration of chlorobenzene

Fig. 5 shows the effect of reaction time on the yield (%) of nitrated products catalysed by 15WZR750 sample with and without any solvent. It can be seen from the plot that a plateau is attained in a very short time of reaction (15 min) when carried out without any solvent. The yield does not increase much with further increase in the reaction time even up to 1 h. However, for reaction in the presence CCl$_4$ it is observed that there is a gradual increase in the yield up to 30 min and there after no much increase in the yield is noticed. In addition, from the plot it can be seen that the activity curve obtained without any solvent is always above the curve obtained in presence of solvent (CCl$_4$). From the above observation, it is understood that the reaction at room temperature and in the presence of solvent (CCl$_4$) proceeds slowly and the yield obtained for a same interval of time is less compared to reaction without any solvent. One of the suspected reason for the saturation in activity of the catalysts could be presumably due to the decomposition of the acetyl nitrate
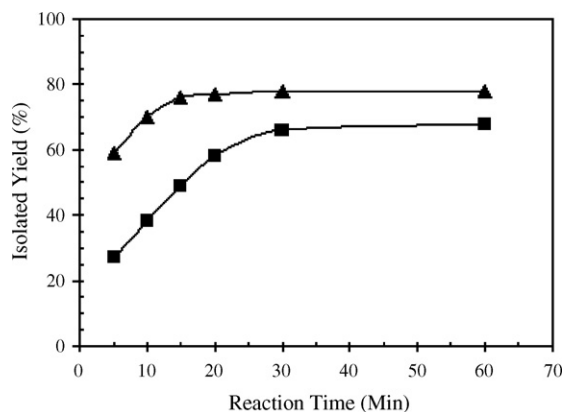

Fig. 5. Effect of reaction time on percentage yield of nitrated product. (–▲–) 15WXR750 without solvent; (–■–) 15WZR750 with CCl$_4$. Catalyst: 0.5 g, 10 mmol chlorobenzene and equivalent quantities of acetic anhydride and nitric acid, 10 ml of CCl$_4$ at room temperature.

must be taking place with time and is not available for nitration reaction.

3.3.4. Effect of sequential addition of reagents

The sequence of addition of various reagents in the reaction has found to affect the yield. The isolated yield increases by 10–12% in the case where the catalyst (WO_x/ZrO_2) was added after the addition of nitric acid and acetic anhydride. However, for all the reaction set up the addition of nitric acid followed by acetic anhydride is always carried out keeping the reaction flask in crushed ice bath to absorb the heat produced due to the exothermic nature of the reaction. The addition of chlorobenzene however, does not affect much irrespective of when it was being added to the reaction mixture.

Our observation as above is contrary to the observation of Smith et al. [9]. In their report they have shown that in the nitration of simple aromatic compounds, the sequence of addition of various reagents does not affect the percentage yield, whereas it affects the selectivity towards different isomeric products, viz. *ortho*-, *para*- and *meta*-substitutions. The catalyst used in this said work was beta zeolite.

In the present study with WO_x/ZrO_2 as catalyst, the higher yield obtained in case where the catalyst was added after the addition of acetic anhydride and nitric acid is not understood very clearly. However, it could be due to the fouling effect of water, available from nitric acid (70%), which might have affect the active sites present on the catalyst surface causing lower yield. The addition of catalyst after the addition of acetic anhydride and nitric acid does not affected by water because the available water consumed by reacting with the excess available acetic anhydride and forms acetic acid.

4. Conclusions

1. The WO_x/ZrO_2 sample prepared by co-precipitation method followed by digestion are influenced by the presence of tungsten species in stabilizing the tetragonal phase.
2. The 15 wt.% W/ZrO_2 is found to be 100% tetragonal phase zirconia up to activation at 750 °C, whereas concentration higher than 15 wt.% W shows the presence of monoclinic WO_3 and below it shows the presence of monoclinic zirconia.
3. The tungsten modification on zirconia not only stabilizes the tetragonal phase but also stabilises its specific surface area. Up to 15 wt.% W there is an increase in surface area, which decreases on further increase in concentration. The possible formation of WO_3, as indicated from XRD pattern may be the reason for the decrease in surface area.
4. The surface acidity of the WO_x/ZrO_2 samples shows similar trend as that of surface area and the reason also probably the same. The NH_3 TPD confirms the presence of acid sites with varying strength from the broad desorption profile. Further it has been found out that 15 wt.% W and activated at 750 °C results maximum acidity of the sample.
5. As like $SO_4{}^{2-}/ZrO_2$ the WO_x/ZrO_2 samples are also found to be efficient for the mononitration of chlorobenzene. Though the activities of WO_x/ZrO_2 are less compared to

$SO_4{}^{2-}/ZrO_2$, the selectivity to *para*-isomer found similar. This indicates the presence of sufficient number of Lewis acid sites along with Brønsted acid sites over WO_x/ZrO_2.
6. The 15 wt.% W loaded sample is found to show highest activity compared to samples having higher or lower concentration. Also, activation of the samples at 750 °C yields more than that of 650 °C activated samples.
7. The detail study of the reaction reveals the effect of various parameters on catalytic activities. It is observed that reaction in solvent free medium yields more compared to in the presence of solvent (CCl_4). Among RT (28 °C), 50 and 70 °C, reaction at 50 °C yields the highest.
8. Reaction carried out for a longer duration does not yield more. Within 30 min of reaction it approaches saturation yield. The reason could be the decomposition of acetyl nitrate with time.

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