



Synthesis, characterization and benzylation activity of nanocrystalline chromia loaded sulfated titania prepared via sol–gel route

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Abstract

Chromia loaded sulfated titania has been synthesized via sol–gel route with different chromia loadings. These catalysts are characterized using conventional techniques such as XRD analysis, FTIR analysis, surface area and pore volume measurements, EDX, SEM and UV–Vis diffuse reflectance spectral analysis. Acidity is measured using spectrophotometric monitoring of adsorption of perylene, thermogravimetric desorption of 2,6-dimethylpyridine and temperature programmed desorption of ammonia. Activity studies are done in the liquid phase. It has been concluded that Lewis acid sites are responsible for the benzylation of arenes with benzyl chloride.

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1. Introduction

The synthesis of metallic oxides by the sol–gel process is presently widely accepted method for the preparation of such materials, in particular when it is desired to incorporate other metallic ions in the gels [1–3]. Several important features characterize these solids, which make them differ considerable from those prepared by more conventional methods. Sol–gel processing enables materials to be mixed on an atomic level and thus crystallization and densification to be accomplished at a much low temperature. The advantages of the sol–gel process in general are high purity, homogeneity and low temperature. For a lower temperature process, there reduced loss of volatile components and thus

the process is more environmental friendly. The final properties shown by these materials depend on the hydrolysis conditions, the pH of the gelling solution, the nature of the salt added before gelling [4]. When titania is prepared by sol–gel method, it can be obtained with a crystallite size in the range of nanometers. The chemical and catalytic properties of titania can be modified by the incorporation of metallic ions. Sulfated metal oxides are strong solid acids that have recently become the focus of much interest. Titania, classified as a solid acidic oxide in both the anatase and rutile crystallographic forms, has long been known to possess catalytic activity, although anatase was found to be more active than rutile [5]. The use of sulfated metal oxides is of increasing interest because of the enhanced chemical properties imparted by the presence of sulfate groups [6,7]. Alkylation of benzene with isopropanol over sulfated titania is already reported [8]. The Friedel–Crafts alkylation reaction is a very useful tool for the synthesis of alkyl aromatic compounds both in laboratory and on an industrial scale, which is

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catalyzed by both Brønsted and Lewis acid centers [9]. The environmental problems due to the use of the ubiquitous catalysts of Friedel–Crafts reaction – AlCl_3 , BF_3 , etc., have aroused for many years a great interest for alternative solutions [10], and this challenge continues to attract the attention of chemists. For this purpose, a large number of catalytic systems including clays, [11] zeolites [12] supported [13] or unsupported transition metal salts [14] and main group metals salts [15] have been widely investigated. In recent years, the use of heterogeneous catalysts in liquid phase reactions has greatly increased due to their advantages such as high activity and selectivity, reusability, ease of separation, no corrosion or disposal of effluent problems, etc. [16]. This paper is concerned with the effect of sulfation and Cr content on the catalytic performance of the prepared system in the benzylation of arenes. The detailed characterizations of the catalysts are also reported.

2. Experimental

The nanocrystalline titania catalysts (T) reported in this study have been prepared by sol–gel method using titanium isopropoxide (Aldrich 98%). When 25 mL $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was hydrolyzed in 300 mL water containing 2.5 mL nitric acid, precipitation occurred immediately. Precipitate were stirred continuously at room temperature to form a highly dispersed sol. To this calculated amount of chromium nitrate solution was added to obtain chromia loaded samples. After keeping the sol for aging it was concentrated and dried at 60 °C. Sulfation was done using 0.5 M sulfuric acid solution (2 mL g^{-1} of the hydroxide). The metal loading was varied from 3% to 12% as indicated by the number in the sample notation. The samples, after overnight drying at 110 °C, were calcined for 5 h at 500 °C.

Powder X-ray diffraction (XRD) patterns have been recorded on a Rigaku D-max C X-ray diffractometer using Ni filtered $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$). Micromeritics Gemini-2360 surface area analyser was used to determine the BET surface area and pore volume under liquid N_2 temperature using N_2 gas as the adsorbent. Thermal analysis between room temperature and 800 °C were carried out in N_2 atmosphere with a ramp of 20 °C min^{-1} using a TGAQ V2.34 thermal analyzer (TA instruments make). FTIR spectra were recorded on a Nicolet Impact 4000 instrument in the range of 4000–400 cm^{-1} on KBr phase. Quantitative elemental analysis of the samples was done by EDX measurements using EDX-JEM-35 instrument (JEOL Co. link system AN-1000 Si–Li detector). Diffuse reflectance UV–Vis spectra of the samples were recorded at room temperature between 200 and 800 nm using MgO as standard in the Ocean Optics AD 2000 instrument with CC detector. The total acidity of the

samples were determined by temperature programmed desorption of ammonia (NH_3 -TPD). For this, pelletised samples were activated inside the reactor under a N_2 flow for half an hour. After cooling to the room temperature, NH_3 was injected in the absence of the carrier gas flow and allowed to attain equilibrium. The excess and physisorbed ammonia was flushed out by a current of N_2 . The temperature was then raised in a stepwise manner employing a linear heating rate of about 20 °C min^{-1} . The ammonia desorbed at each temperature at an interval of 100 °C was collected in dilute sulfuric acid and estimated. Electron acceptor studies [17] were carried out by stirring a weighed amount of the catalyst with perylene solutions of different concentrations, benzene being used as the nonaqueous medium. The amount of perylene adsorbed was determined spectroscopically by measuring the absorbance of the solution in a UV–Vis spectrophotometer (Shimadzu UV-160 A) before and after adsorption. The limiting amount of perylene adsorbed was obtained from the Langmuir plots. The acidity determination was supported by the TGA studies using 2,6-dimethylpyridine (DMP) as a probe molecule. Previously activated catalysts were kept in a dessicator saturated with vapours of 2,6-DMP at room temperature for 48 h and then subjected to thermal analysis in N_2 atmosphere at a heating rate of 20 °C min^{-1} . Their fraction of weight loss in the range 300–600 °C was found out and taken as a measure of the Brønsted acidity of the samples.

The reaction between toluene and *o*-xylene using benzyl chloride was carried out in liquid phase in a round-bottom 50 mL double-necked flask, provided with a magnetic stirrer, a thermometer and a spiral condenser. The temperature was maintained using an oil bath. In a typical reaction procedure, substrate and benzyl chloride in the specific molar ratio was added to 0.1 g of the catalyst in the round bottom flask and the reaction mixture was magnetically stirred. The products were identified by gas chromatography (Chemito 8610), N_2 carrier gas, injection port temperature 230 °C, column temperature 80 °C, at a heating rate of 3 °C, detector temperature 250 °C using SE-30 column and FID detector. The reaction always yielded a single product under the present reaction conditions and is named as monoalkylated product (MAP). The catalytic activity was expressed as the percentage conversion (wt%) of benzyl chloride. The effect of reaction temperature, reaction time, catalyst concentration and substrate to benzyl chloride molar ratio on the catalyst performance was examined in order to optimize the conversion of benzyl chloride and selectivity to the monoalkylated product. The present work also attempts a closer look into the metal leaching and deactivation of the systems under the reaction conditions to obtain a better understanding of the nature and course of the reaction.

3. Results and discussion

X-ray diffraction patterns of the sample calcined at 500 °C are shown in Fig. 1. XRD was used for crystal phase identification and the crystallite size of each phase present. The XRD intensities of the anatase (101) peak at $2\theta = 25.5^\circ$ and the rutile (110) peak at 27.5° were analyzed [18]. The average crystallite size was determined using Scherrer equation [19]. It has been reported that the degree of crystallization of the sulfated oxides is much lower than that of the oxides without sulfate treatment [20]. Sulfation retards the transformation from anatase to rutile in comparison with the sample without sulfation. In addition to stabilizing anatase TiO_2 crystallites, sulfate surface species inhibit TiO_2 crystallite sintering leading to lower crystallite than in pure TiO_2 . The bulk structure of titania remains virtually unchanged by the incorporation of chromia, except for a lowering in crystallinity. The absence of characteristic peaks of chromia implies the high dispersion of chromium particles on the titania surface. The sulfate content as obtained by EDX analysis is presented in Table 1. Incorporation of chromium significantly improves the sulfate retaining ability. It may be assumed that the dispersion of chromium particles restricts the sulfate species more or less to the surface, minimizing their migration into the bulk.

The surface area of chromia loaded samples is higher than that of pure titania calcined at that temperature (Table 1). Sulfation reduces the extent of surface area loss during high temperature calcinations. The sulfated samples showed a higher surface area compared to pure titania. This can be explained on the basis of higher resistance to sintering as well as the delayed transformation from amorphous to crystalline state acquired by doping with sulfate ions [20,21]. FTIR spectra (Fig. 2) of the systems shows a peak at $1200\text{--}1100\text{ cm}^{-1}$ which can be assigned to S=O group [22]. The peak around 1400 cm^{-1} suggests that the added sulfate exists as SO_4^{2-} species. The bands around 1636 and 3436 cm^{-1}

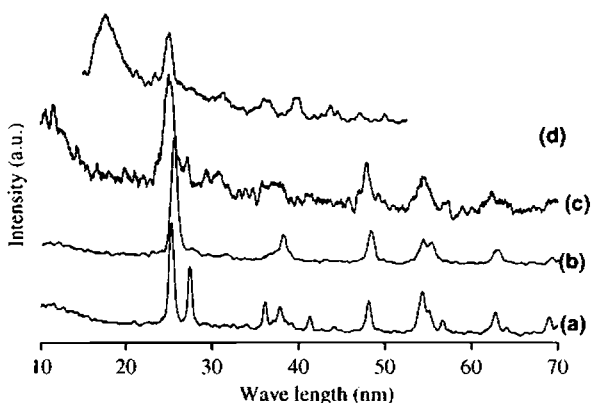


Fig. 1. XRD profiles of: (a) T, (b) ST, (c) STCr3, (d) STCr9.

correspond to the bending and stretching modes of the --OH groups present in the catalysts. Thermal analysis of the samples showed an initial weight loss in the range of $90\text{--}150^\circ\text{C}$ and this could be attributed to the removal of surface adsorbed water. The weight loss in the temperature range $650\text{--}750^\circ\text{C}$, is due to the decomposition of the sulfate species and evolution of oxides of sulfur [23]. UV-Vis diffuse reflectance spectroscopy (Fig. 3) permits the detection of framework Ti in the samples. Characteristic band for tetrahedrally coordinated titanium appears at about $300\text{--}400\text{ nm}$. A progressive shift in the band gap absorption onset to the visible region and a decrease absorbance in UV region were noticed with increasing Cr content. The absorption is associated to the $\text{O}^{2-} \rightarrow \text{Ti}^{4+}$ charge transfer corresponding to electronic excitation from the valence band to the conduction band. Scanning electron micrographs of the representative samples are shown in Fig. 4, which clearly gives the surface morphologies.

The ammonia TPD results (Table 2) indicate that the number of acid sites on pure titania is much less compared with that of sulfated titania and chromic loaded systems. The number and strength of all types of acid sites namely, weak, medium and strong are increased by gradually increasing the chromium oxide content upto 6 wt% which then declines. The increase enhancement of acidity can be attributed to the increase of the electron accepting properties of the three coordinated metal cations via the inductive effect of the sulfate anions, which withdraw electron density through the bridging oxygen atom [24]. The reduction in the acidity values for high chromia containing sulfated systems may be owing to the higher amount of sulfate retained on the surface. Elemental analysis by EDX revealed that amount of sulfate retained is higher for STCr9 and STCr12. The decrease in surface acidity at high concentration of sulfate is probably due to the formation of polysulfate, which reduces the number of Brönsted sites and consequently that of the total acid sites [25]. Adsorption studies using perylene as electron donor gives information regarding the Lewis acidity in presence of Brönsted acidity [26,27]. The technique is based on the ability of the catalyst surface site to accept a single electron from an electron donor like perylene to form charge transfer complexes. Perylene after electron donation gets adsorbed on the catalyst surface as radical cation. The limiting amount of perylene adsorbed, which gives a measure of the Lewis acidity or the electron accepting capacity, was obtained from the Langmuir plot. Pure titania shows adsorption which indicates lower electron accepting capacity and hence the lower Lewis acidity. As the electronegativity of the incorporated chromium ions is higher than that of Ti, an increase in Lewis acidity is expected in all the cases. At high chromia loadings a significant loss of Lewis acid sites is apparent from the perylene adsorption results.

Table 1
Surface parameters of the prepared systems

Catalyst	Surface area BET ($\text{m}^2 \text{g}^{-1}$)	Pore volume (cc g^{-1})	Crystallite size (nm)	Pore diameter (nm)	Elemental composition from EDX (%)		
					TiO ₂	SO ₄	Cr
T	35	0.09	12.71	102.8	100	–	–
ST	91	0.21	9.62	92.3	95.34	4.66	–
STCr3	100	0.18	5.90	72.0	88.05	9.16	2.78
STCr6	123	0.17	6.16	55.3	83.59	10.52	5.90
STCr9	128	0.17	6.38	53.1	81.60	10.58	7.82
STCr12	137	0.15	9.84	43.8	74.23	14.70	11.07

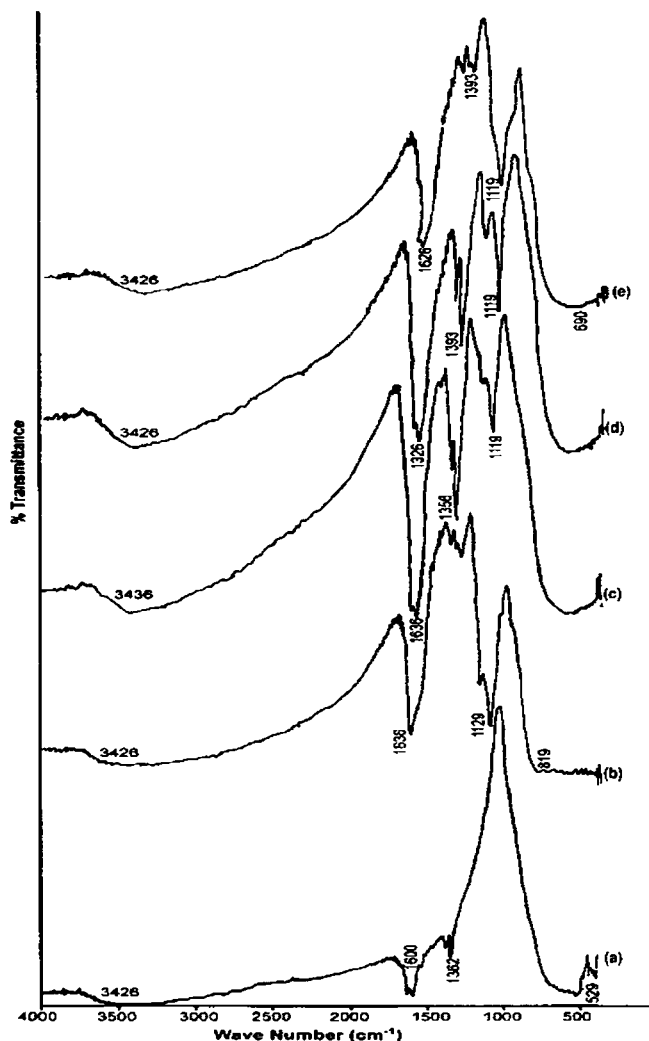


Fig. 2. FTIR spectra of: (a) T, (b) ST, (c) STCr3, (d) STCr6, (e) STCr9.

This may be due to the high sulfate loading which exists in the form of polynuclear pyrosulfates [28]. The thermodesorption study of 2,6-DMP was carried out with an intention of obtaining a comparative evaluation of the Brønsted acidity in the samples. Satsuma et al. [29] reported a complete elimination of the coordinatively

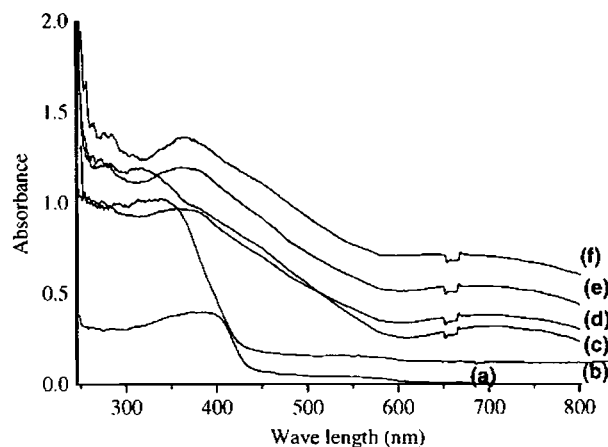


Fig. 3. Diffuse reflectance UV-Vis spectra of: (a) T, (b) ST, (c) STCr3, (d) STCr9, (f) STCr12.

adsorbed 2,6-DMP after purging at an appropriate temperature (above 300 °C). Thus, we presume the amount of 2,6-DMP desorbed at temperatures above 300 °C to be due to desorption from Brønsted acid sites and the results are represented in Fig. 5.

A series of tests was made to determine how the important process parameters influenced the benzylation reaction (Table 3). We made the reaction run using benzyl chloride and toluene in the absence of a catalyst (blank run) and in the presence of the catalyst (0.1 g STCr3) at the refluxing temperature of the mixture. We observed a percentage conversion of 2.1 and 88.1% after 60 min of reaction in the absence and presence of the catalyst, respectively. Low yield for the reaction in the absence of the catalyst is due to the higher activation energy of the uncatalysed reaction. Addition of the catalyst significantly reduced the activation energy and the reaction proceeds through a different path with a lower activation energy, resulting in a higher percentage conversion. The variation of benzyl chloride conversion and product selectivity as a function of temperature was investigated in the temperature range 70–110 °C over STCr3 catalyst. The benzyl chloride conversion is found to increase gradually with the rise in temperature. This is probably due to the speedy desorption of the alk-

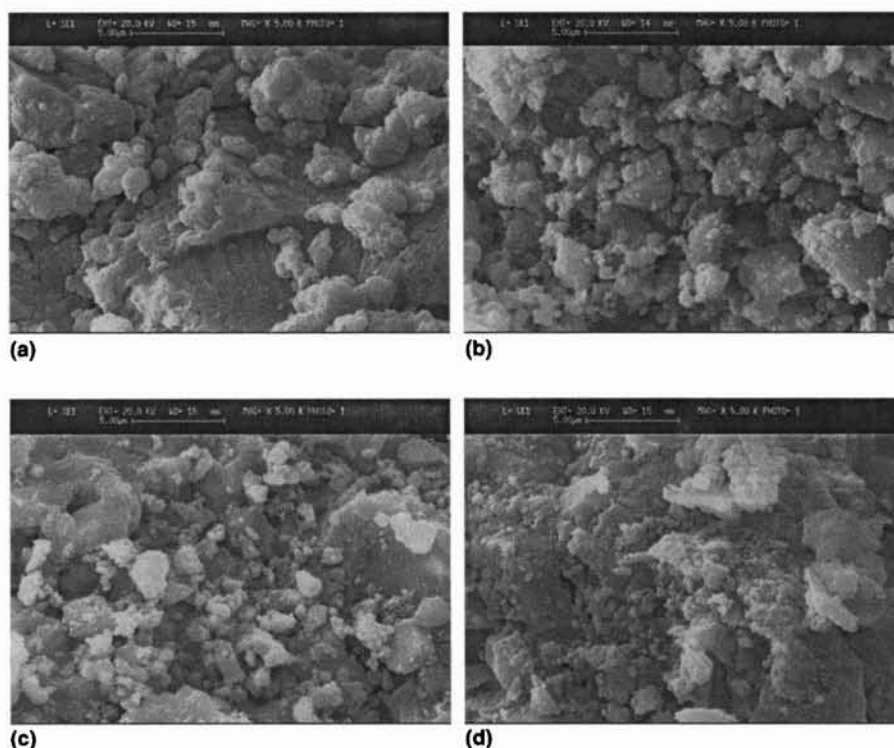


Fig. 4. SEM of: (a) T, (b) ST, (c) STCr3, (d) STCr9.

Table 2
Surface acidity obtained from ammonia TPD and the conversion of benzyl chloride

Catalyst	Substrate		Amount of ammonia desorbed (mmol g^{-1})			
	Toluene ^a Conversion (wt%) ^a	<i>o</i> -Xylene ^b	Weak (100–200 °C)	Medium (200–400 °C)	Strong (400–600 °C)	Total (100–600 °C)
T	33.6	38.6	0.3108	0.2019	0.0103	0.5230
ST	83.4	70.8	0.5010	0.3221	0.0895	0.9126
STCr3	88.1	80.8	0.5620	0.5924	0.2898	1.4442
STCr6	91.4	93.8	0.7532	0.6745	0.3096	1.7373
STCr9	68.9	89.4	0.4202	0.4704	0.0188	0.9094
STCr12	65.2	63.8	0.4254	0.4353	0.0176	0.8783

^a Substrate: benzyl chloride, 10:1; amount of catalyst, 0.1 g; reaction time, 1 h; reaction temperature: ^a110 °C, ^b90 °C.

ylated product from the catalyst surface. Maximum conversion is found to be at the refluxing temperature with 100% selectivity to the monoalkylated product. A continuous increase in the percentage conversion of benzyl chloride is registered with increase in reaction time, which confirms the heterogeneity of the catalytic reaction. In heterogeneous catalysis the amount of catalysts plays an important role in determining the rate of the reaction. Taking different amounts of STCr3 catalyst and keeping the amount of benzylating agent constant vary the catalyst concentration. The conversion is found to increase with the increase in the amount of the catalyst. The reactivity was scanned for different molar ratios. The conversion of benzyl chloride is increased with increase in the toluene to benzyl chloride molar ratio. Since the toluene is taken in excess, the reaction is

supposed to proceed via a pseudo unimolecular mechanism. The rate of the reaction should vary with the concentration of the benzyl chloride. The results show that the benzylation is favoured with a lower concentration of benzylating agent. When benzylating agent concentration is high (low toluene to benzyl chloride molar ratio) there may be an enhanced poisoning effect by the alkylated products, which is strongly adsorbed on the catalyst surface. This restricts further adsorption of the reactant molecules and thus reduced the conversion of benzyl chloride.

In order to study the effect of moisture on the catalyst, the catalysts stored in a desiccator saturated with water vapour at room temperature for 48 h were used for benzylation of toluene. The reactions were carried out at 110 °C for 2 h by taking toluene to benzyl

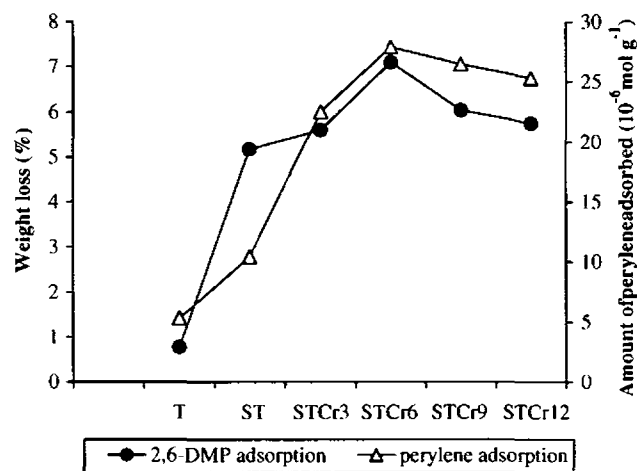


Fig. 5. Thermodesorption studies using 2,6-DMP and perylene adsorption studies.

Table 3
Optimization of different reaction parameters

Parameters	Conversion (wt%)
Temperature ($^{\circ}$C)^a	
70	5.9
80	13.1
90	20.6
100	73.5
110	88.1
Amount of catalyst (g)^b	
–	2.1
0.05	62.6
0.10	78.1
0.15	88.4
0.20	99.2
0.25	100.0
Toluene:benzyl chloride^c	
5:1	49.9
10:1	88.1
15:1	89.6
20:1	95.6
25:1	100.0
Time (min)^d	
30	62.3
60	88.1
90	89.4
120	90.8
150	91.6
180	95.7

^a Toluene: benzyl chloride: 10:1, reaction time, 1 h; amount of catalyst, 0.1 g; STCr3.

^b Toluene: benzyl chloride: 10:1, reaction time, 1 h; reaction temperature, 110 $^{\circ}$ C.

^c Reaction time, 1 h; reaction temperature, 110 $^{\circ}$ C; amount of catalyst, 0.1 g; STCr3.

^d Toluene: Benzyl chloride: 10:1, reaction temperature, 110 $^{\circ}$ C; amount of catalyst, 0.1 g; STCr3.

chloride molar ratio 10:1. For comparison parallel runs were conducted using fresh catalysts. The percentage conversion suddenly raised from 15.7 to 59.3 in the time

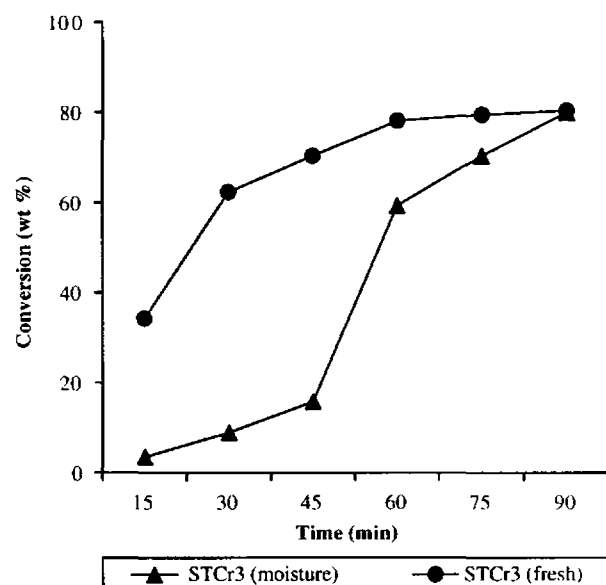


Fig. 6. Effect of moisture on the conversion of benzyl chloride over STCr3.

range of 45–60 min (Fig. 6). Thus, there was a time period for which the catalyst was inactive towards reaction, when it is adsorbed with moisture. However, after the induction period, reaction proceeds with almost the same rate. The moisture gets adsorbed on the active sites on the catalyst surface and prevents the interaction of benzyl chloride molecules with these sites. Once the sites are freed from moisture, they are active towards the desired reaction. These catalysts do not demand stringent moisture-free conditions for them to be highly active in benzylation process. The reusability of the catalyst systems was also subject to investigation. The catalyst was removed by filtration from the reaction solution, washed thoroughly with acetone, dried and then activated. No pronounced change was observed in the XRD pattern, except for a slight lowering of intensity, symptomatic of the retention of the crystalline nature. It was tested for catalytic activity and only a slight decrease in activity was observed. This suggests the resistance to rapid deactivation. To prove the heterogeneous character of the reactions, the solid catalyst was removed by filtration after a particular time from the reaction mixture at the reaction temperature and the filtrate was again subjected for reaction for 30 more min. The filtrate was further subjected to qualitative analysis for testing the presence of leached metal ions. From the results it is clear that chromium ions are not leaching from the metal oxide surface during benzylation reaction. No noticeable change in conversion could be detected, indicating the absence of metal leaching. The reaction was done under the optimized conditions and the results are given in Table 2, which can be correlated to the acidity of the samples. In order to know the substrate effect,

we had conducted the reaction between *o*-xylene and benzyl chloride. It was found that the reaction is much faster and gives good conversion at 90 °C itself. At 110 °C all catalysts gives 100% conversion. –CH₃ being an electron-donating group, will increase the electron density on the benzene ring and makes it more vulnerable to the attack by an electrophile [30]. Thus it is worth mentioning that the reactivity of aromatic nucleus increases with the number of electron donation groups attached to the aromatic ring. Hence *o*-xylene, which has two methyl groups, reacts more easily than toluene with only one methyl group.

The alkylation of toluene and *o*-xylene with benzyl chloride can be successfully carried out in the presence of chromia loaded sulfated titania catalyst, with 100% selectivity to monoalkylated product. The prepared systems are environmentally friendly and are easy to handle. The thermal and chemical stability of the systems, along with its high Lewis acidity, reusability and resistance to deactivation, render it a promising catalyst for Friedel–Crafts benzylation reaction.

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