Liquid-phase alkylation of phenol with long-chain olefins over WO$_x$/ZrO$_2$ solid acid catalysts

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Abstract

The liquid-phase alkylation of phenol with 1-dodecene was carried out over WO$_x$/ZrO$_2$ solid acid catalysts. The catalysts were prepared by wet impregnation method using zirconium oxyhydroxide and ammonium metatungstate. Catalysts with different WO$_3$ loading (5–30 wt.%) were prepared and calcined at 800 °C and catalyst with 15% WO$_3$ was calcined from 700–850 °C. All the catalysts were characterized by surface area, XRD, and FTIR. The catalyst with 15% WO$_3$ calcined at 800 °C (15 WZ-800) was found to be the most active in the reaction. The effect of temperature, molar ratio and catalyst weight on dodecene conversion and products selectivity was studied in detail. Under the optimized reaction conditions of 120 °C, phenol/1-dodecene molar ratio 2 and time 2 h, the catalyst 15 WZ-800 gave >99% dodecene conversion with 90% dodecylphenol selectivity. Comparison of the catalytic activity of 15 WZ-800 with sulfated zirconia calcined at 500 °C (SZ-500) and Hβ zeolite showed that activity of SZ-500 was lower than that of 15 WZ-800, while Hβ zeolite showed negligible activity. It is observed that the presence of water in the reaction mixture was detrimental to the catalytic activity of WO$_x$/ZrO$_2$. The catalyst 15 WZ-800 also found to be an efficient catalyst for alkylation of phenol with long-chain olefins like 1-octene and 1-decene.
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Keywords: Zirconia; Tungsten oxide; Alkylation; Phenol; Long-chain olefins

1. Introduction

The alkylation of phenol with alcohols and olefins are industrially important as it is used for the production of a variety of products [1] and the reaction is studied under a variety of catalysts and conditions [2–5]. Alkylation of phenol with 1-dodecene is important as it is used for the production of dodecylphenol, a dense viscous, light yellow liquid with the characteristic smell. Dodecylphenol is used as raw material for manufacturing lubricant additives, anionic detergents, antioxidants, and in phenol resins, adhesives, paints and accelerator for curing epoxy resins. Most of the information in connection with this reaction is available in the form of patent literature.

Conventionally this reaction is carried out by the reaction of phenol with 1-dodecene in presence of cation-exchange resin. Though, cation-exchange resin catalysts are environmentally friendly, they have the disadvantage of low stability at high temperatures [6]. Therefore, considerable efforts have been made for the development of suitable heterogeneous catalysts. The catalysts reported for this reaction includes sulfated zirconia, zeolites, and immobilized ionic liquids [7–9].

Zirconia based solid acids are attracting much attention in recent years. For instance, sulfated zirconia proved to be a highly active solid acid catalyst for various organic transformations [10]. But, its poor stability and tendency to form volatile sulfur compounds during catalysis and regeneration limit its applicability [11]. However, zirconia-supported tungsten oxide, WO$_x$/ZrO$_2$ is shown to be an alternative to sulfated zirconia, which is stable at high temperature and in presence of both oxidizing and reducing atmosphere [12,13].

The present work deals with the alkylation of phenol with 1-dodecene using WO_x/ZrO_2 as the catalyst. The reaction was carried out with an aim to maximize olefin conversion together with the selectivity to alkylphenol. The influence of WO_3 loading and catalyst calcination temperature on dodecene conversion and product selectivity were studied. The catalyst with highest activity was used to study various reaction parameters such as temperature, molar ratio and catalyst weight. The study further extended to the comparison of 15 WZ-800 with SZ-500 and Hβ zeolite in phenol alkylation with 1-dodecene, Alkylation of phenol with olefins like 1-octene and 1-decene were also studied using 15 WZ-800 catalyst.

2. Experimental

2.1. Chemicals

Zirconium oxychloride ($ZrOCl_2·8H_2O$) and ammonia (25%) were procured from S.D. Fine Chemicals Ltd., Mumbai. Phenol was obtained from Merck (India) Ltd., Mumbai. Ammonium metatungstate hydrate (($NH_4)_6H_2W_{12}O_{40}·xH_2O$), 1-dodecene, 1-decene, and 1-octene were purchased from Aldrich. Sulfated zirconia was obtained from MEL Chemicals and zeolite Hβ (Si/Al = 40) was procured from PQ Corporation. All the chemicals were research grade and used as received, without further purification.

2.2. Catalyst preparation

The catalysts were prepared by wet impregnation method using zirconium oxyhydroxide as the support and ammonium metatungstate as tungsten precursor. The support was prepared by the hydrolysis of an aqueous solution of zirconium oxychloride with aqueous NH_3. The precipitate obtained was washed till free from chloride and dried at 120 °C. To an aqueous solution of ammonium metatungstate, zirconium oxyhydroxide powder was added and the mixture was stirred for 8–10 h. The excess of water was evaporated to dryness and the product obtained was dried at 120 °C and calcined in air at different temperatures. A series of catalysts with different WO_3 loading (5–30 wt.% of zirconium oxyhydroxide) were prepared and calcined at 800 °C. In order to study the influence of calcination temperature on catalytic activity, the 15% WO_3/ZrO_2 catalyst was calcined from 700–850 °C. The catalysts are represented by *x* WZ-*T* where, *x* represents wt.%, W represents WO_3, Z represents ZrO_2 and *T* denotes calcination temperature in °C.

2.3. Characterization

The specific surface area of the catalysts were measured by N_2 physisorption at liquid nitrogen temperature using a Quantachrome Nova-1200 surface area analyzer and standard multi point BET analysis methods. Samples were dried at 300 °C in N_2 flow for 2 h before N_2 physisorption measurements.

X-ray diffraction (XRD) measurements of the catalyst powder were recorded using a Rigaku Geigerflex diffractometer equipped with Ni filtered Cu Kα radiation ($\lambda = 1.5418$ Å). The volume percentage (vol.%) of the tetragonal phase (V_t) of the catalyst samples were estimated using the formula proposed by Toraya et al. [14],

$$X_m = \frac{I_m(1\,1\,-1) + I_m(1\,1\,1)}{[I_m(1\,1\,-1) + I_m(1\,1\,1) + I_t(1\,1\,1)]}$$

$$V_m = \frac{1.311\,X_m}{1 + 0.31X_m} \text{ and } V_t = 1 - V_m$$

where I_m ($h\,k\,l$) is the integral intensity of the ($h\,k\,l$) reflections of the monoclinic phase and I_t ($1\,1\,1$) the intensity of the ($1\,1\,1$) reflection of the tetragonal phase.

The FTIR spectra of the samples were recorded on a Shimadzu (Model-820 PC) spectrophotometer under DRIFT (diffuse reflectance infrared Fourier transform) mode.

2.4. Catalytic activity

The liquid-phase alkylation of phenol with 1-dodecene was carried out under atmospheric pressure in 50 ml glass batch reactor fitted with reflux condenser and $CaCl_2$ guard tube. The temperature was controlled by means of a thermostatic oil bath in which the glass reactor was immersed. The catalyst was activated at 500 °C for 2 h in flow of dry air and cooled to the reaction temperature prior to its use in the reaction. In a typical run, 10 g of the reaction mixture was taken in the batch reactor and the required quantity of the catalyst was added and the reaction mixture was heated under constant stirring. The clear solution of the reaction mixture was withdrawn periodically, centrifuged and analyzed by Shimadzu 14B gas chromatograph, equipped with a FID detector using HP-5 capillary column (cross linked 5% ME silicone, 30 m × 0.53 μm × 1.5 μm film thickness). The products were confirmed by GC–MS and IR spectroscopy.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. Surface area

Pure ZrO_2 calcined at 800 °C has low surface area, 10 $m^2\,g^{-1}$ (Table 1) and its surface area increased with WO_3 loading and reached maximum at 15% WO_3 (61 $m^2\,g^{-1}$). This can be explained as the added WO_3 forms a surface over layer that reduces the surface diffusion of zirconia and inhibits sintering and stabilizes the tetragonal phase of zirconia, which leads to an increase in surface area [15]. Above

Table 1
Surface area, surface density and phase composition of various catalysts

Sample	Surface area $(m^2\,g^{-1})$	Surface density $(W\,nm^{-2})$	vol.% t-ZrO_2
Z-800	12	0	6
5 WZ-800	38	3.9	9
10 WZ-800	54	5.5	66
15 WZ-800	61	7.3	93
20 WZ-800	55	10.9	89
25 WZ-800	50	14.9	96
30 WZ-800	48	18.7	95
15 WZ-700	84	5.3	100
15 WZ-750	70	6.4	95
15 WZ-850	44	10	19

15% WO_3 loading, the formation of crystalline WO_3 (see Section 3.1.2) probably narrows or plugs pores of the samples, thus leading to the decrease in the specific surface area [16].

The nominal WO_3 loading corresponding to each loading and calcination temperature was determined to calculate the tungsten (W) surface density using the measured surface area. The tungsten surface densities, expressed as the number of W atoms per nanometer square area (W atoms nm^{-2}), were calculated using the equation, surface density of W = {[WO_3 loading (wt.%)/100] × 6.023 × 10^{23}}/{[231.8 (formula weight of WO_3) × BET surface area ($m^2\,g^{-1}$) × 10^{18}]} and are given in Table 1. The values indicate that W surface density increased with WO_3 loading and calcination temperature and the increase in surface density with calcination temperature is due to the concomitant decrease in the ZrO_2 surface area (Table 1).

3.1.2. X-ray diffraction

Pure ZrO_2 calcined at 800 °C exist mainly in monoclinic form and as the WO_3 loading increased, ZrO_2 crystallized progressively into tetragonal form and at 15% WO_3 loading ZrO_2 exist mainly in the tetragonal form (Fig. 1). The tetragonal content of zirconia at a fixed loading depends on the calcination temperature and for 15% catalyst, zirconia exists mainly in the tetragonal form up to 800 °C and decreases with further increase in calcination temperature (Table 1). At high calcination temperature, WO_x species agglomerate into monoclinic WO_3 crystallites and becomes less effective sintering inhibitors. It can also be seen that up to a 10% WO_3 loading for catalysts calcined at 800 °C and for 15% catalyst, up to 750 °C calcination, no XRD peaks corresponding to crystalline WO_3 were observed, indicating WO_3 is highly dispersed on the support surface. However, when WO_3 loading was higher than 10%, or when the calcination temperature exceeds 750 °C for 15% loading, new peaks appeared in the 2θ region of 23–25°, characteristic of monoclinic WO_3 [17]. Thus, when the W surface density exceeds the theoretical monolayer capacity of ZrO_2 (7 W nm^{-2}) i.e., WO_3 loading exceeds monolayer coverage, XRD spectra showed the presence of bulk crystalline WO_3.

3.1.3. FTIR spectroscopy

The catalyst with different WO_3 loading and calcination temperature were characterized by FTIR spectroscopy (Fig. 2). The catalyst 20 WZ-800 showed three distinct bands centered at about 791, 992, 1110 cm^{-1}. The band at 791 cm^{-1} was assigned to a W–O vibration possibly comes from both crystalline and non-crystalline species [18]. The band at 1110 cm^{-1} is due to the presence of monoclinic WO_3 phase, and the band at 992 cm^{-1} is due to a polytungstate
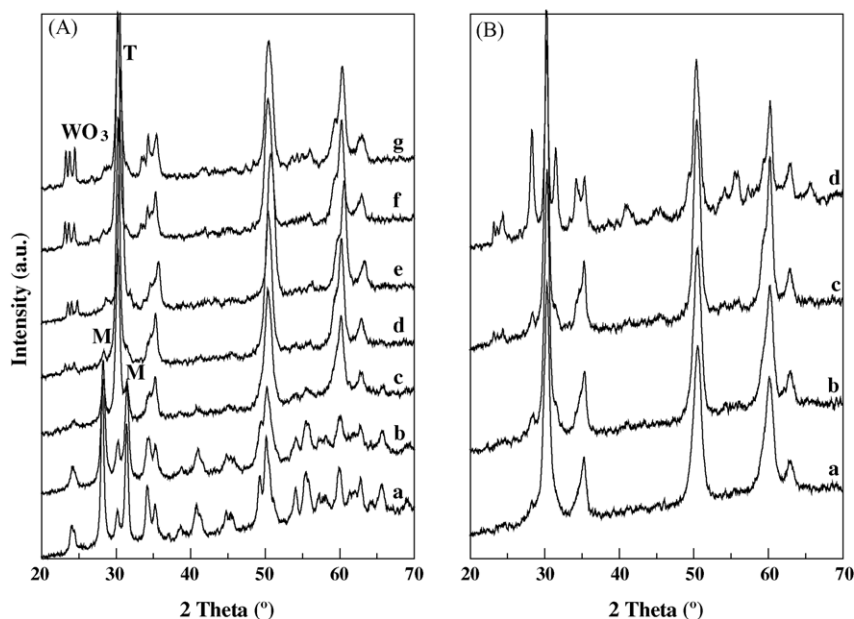

Fig. 1. XRD patterns of (A) (a) ZrO_2, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25, and (g) 30 WZ-800 catalysts and (B) 15 WZ calcined at (a) 700 °C, (b) 750 °C, (c) 800 °C, and (d) 850 °C.
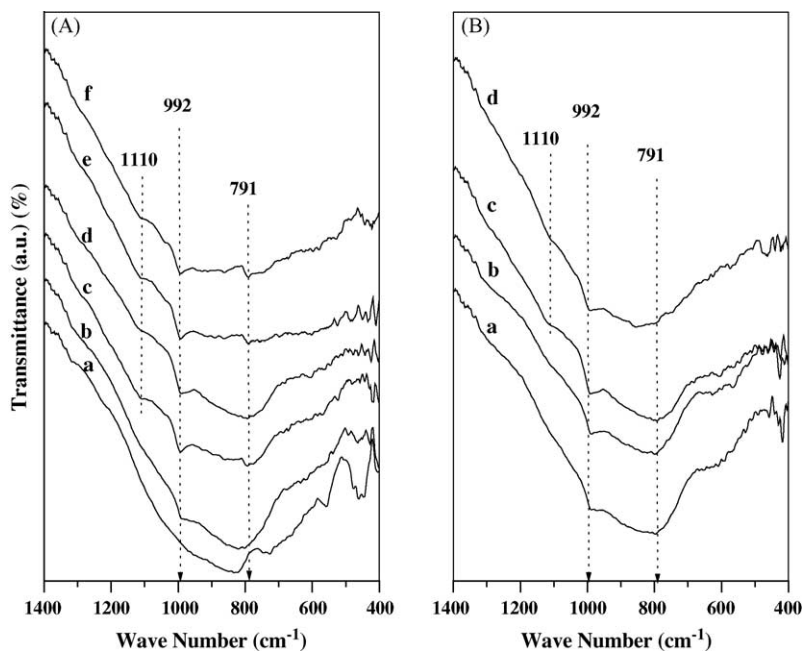
Fig. 2. FTIR spectra of (A) (a) 5, (b) 10, (c) 15, (d) 20, (e) 25, and (f) 30 WZ-800 catalysts and (B) 15 WZ catalyst calcined at (a) 700 °C, (b) 750 °C, (c) 800 °C, and (d) 850 °C.

structure with tungsten in octahedral coordination [19]. This band appeared at lower wave number than those reported in the literature [20,21].

3.2. Catalytic activity

Dodecene undergoes double bond shift isomerization and phenol alkylation in presence of catalyst. The different isomers of dodecene react with phenol to form isomeric mixture of phenyldodecyl ether and dodecylphenol. Analysis of the products by IR spectroscopy showed bands at 752 and 829 cm^{-1} corresponding to the formation of *ortho-* and *para-*dodecylphenol (Fig. 3) [8]. The formation of heavy products
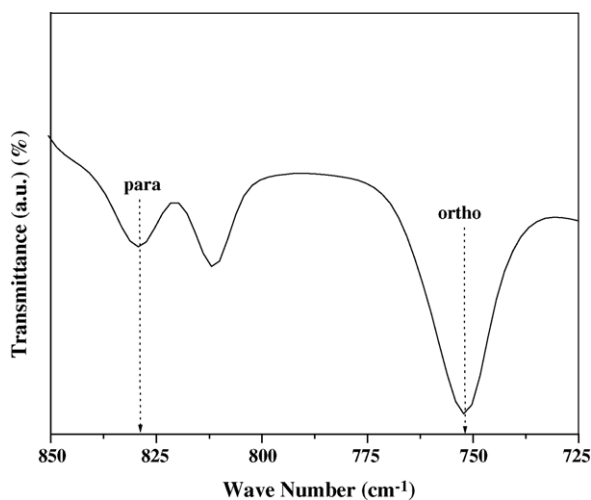

Fig. 3. 1R spectra of phenol/1-dodecene reaction product mixture.

(unidentified) was also indicated at high temperature. The conversion was expressed as the percentage of alkene converted into products.

3.2.1. Effect of WO$_3$ loading

In order to investigate the effect of WO$_3$ loading, on dodecene conversion 5–30 WZ-800 catalysts were used in alkylation of phenol at 70 °C for 2 h (Fig. 4). Pure ZrO$_2$ and 5 WZ-800 showed no activity. Among the catalysts with different WO$_3$ loading, 10 WZ-800 showed the lowest dodecene conversion (9%), and the conversion increased to 67% with 15 WZ-800 catalyst. The catalysts 20 WZ-800 and 25 WZ-800 gave similar conversions as that of 15 WZ-800. Further increase in WO$_3$ loading decreased the dodecene conversion, as for the catalyst 30 WZ-800, the conversion was about 56% after 2 h. The selectivity to different products depended on WO$_3$ loading. The catalyst 10 WZ-800 showed relatively higher selectivity to phenyldodecyl ether and hence lower selectivity to dodecylphenol.

3.2.2. Effect of calcination temperature

The catalyst 15 WZ calcined from 700–850 °C has been used to study the effect of calcination temperature on the catalytic activity. From the results shown Fig. 5, it is clear shows that calcination temperature has a profound effect on the catalytic activity. The catalyst calcined at 700 °C gave 16% dodecene conversion, which increases to 67% with catalyst calcined at 800 °C. The catalyst 15 WZ-700 showed high phenyldodecyl ether selectivity and low alkyl phenol selectivity.

Fig. 6 shows TOF (mol mol^{-1} W s^{-1}) of the catalysts 10–30 WZ-800 and 15 WZ calcined from 700–850 °C as
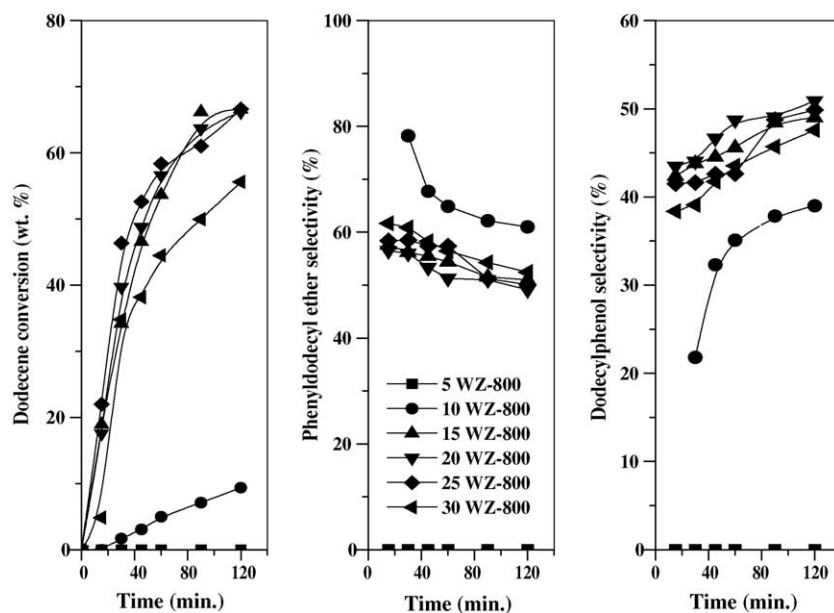
Fig. 4. Effect of WO_3 loading on dodecene conversion and product selectivity. Conditions: temperature = 70 °C, total weight = 10 g, phenol/1-dodecene molar ratio = 2, catalyst weight = 3 wt.%.

a function of W surface density (W nm^{-2}). The catalyst with surface density 7.3 W nm^{-2} has the highest TOF, which is slightly higher than the monolayer coverage of WO_3 on zirconia. Iglesia and co-workers from in situ acidity measurements showed that Brönsted acidity of WZ catalysts increases up to monolayer coverage of WO_3 on zirconia [22]. At high W surface densities, XRD showed the presence of bulk crystalline WO_3 and hence the active sites were inaccessible to

the reactants, which decreased the TOF. The highest catalytic activity at surface density of 7.3 W nm^{-2} clearly indicated that irrespective of WO_3 loading and calcination temperature, catalytic activity depended on WO_3 coverage and the catalyst with WO_3 loading slightly higher than that required for monolayer coverage had the highest catalytic activity.

Since phenol is hydrophilic in nature, it can be contaminated with water. In order to check the role of water on
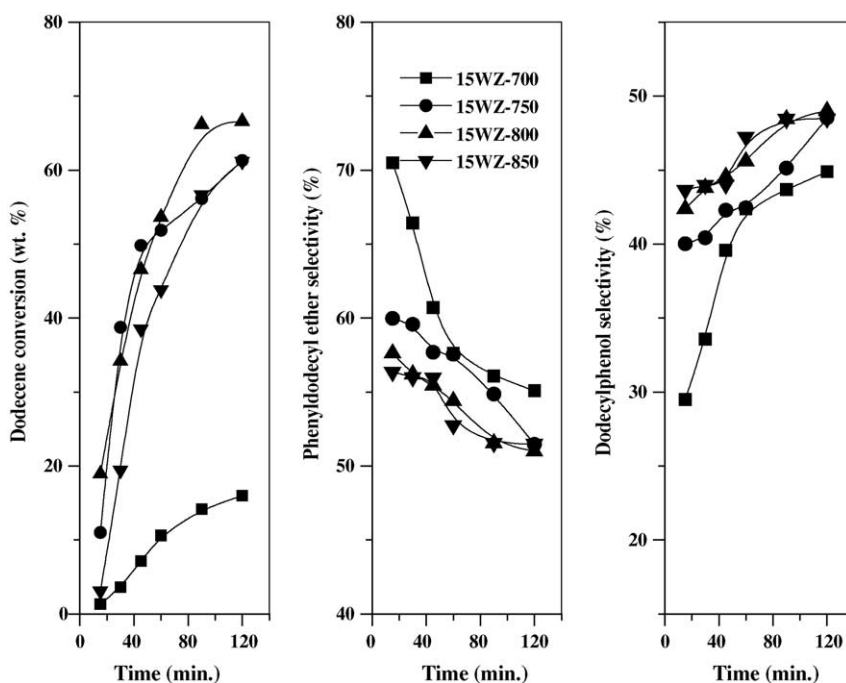

Fig. 5. Effect of calcination temperature on dodecene conversion and product selectivity. Conditions: temperature = 70 °C, total weight = 10 g, phenol/1-dodecene molar ratio = 2, catalyst weight = 3 wt.%.
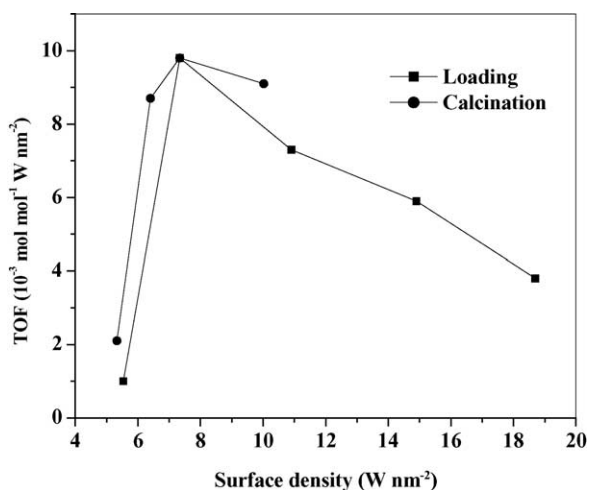
Fig. 6. TOF vs. surface density of catalysts with different WO_3 loading calcined at 800 °C and 15 WZ calcined at different temperatures.

catalytic activity, reaction was studied by the addition of water (0.5 wt.% of total weight of the reaction mixture) to the reaction mixture. In presence of water, no reaction was observed and it could be due to the strong adsorption of water on the catalyst surface, which prevents the accessibility of the reactants to the active sites of the catalyst and thereby inhibits the reaction.

3.2.3. Effect of reaction temperature

The reaction was studied in the range of temperatures from 70 to 120 °C using the most active catalyst 15 WZ-800 (Fig. 7). At 70 °C, dodecene conversion was

67% (2 h) and increased to >99% at 120 °C. The product selectivity varied drastically with reaction temperature. The selectivity to phenyldodecyl ether was high at low reaction temperature (51% at 70 °C) and decreased with an increase in temperature and disappeared at 120 °C. The decrease in phenyldodecyl ether selectivity with temperature was due to its rearrangement to dodecylphenol in presence of catalyst. Formation of heavy products was also observed at temperature >70 °C and its selectivity increased with temperature and reached 10% at 120 °C, in 2 h.

3.2.4. Effect of molar ratio

The effect of molar ratio on dodecene conversion and product selectivity was studied at 70 °C with phenol/dodecene molar ratio 2, 4, and 6 (Fig. 8). As the phenol/1-dodecene molar ratio increased from 2 to 4, dodecene conversion increased (67–79%) and further increase in molar ratio to 6 had no appreciable effect. The selectivity to phenyldodecyl ether was high at phenol/1-dodecene molar ratio of 6 and at lower molar ratios selectivity to different products was similar.

3.2.5. Effect of catalyst weight

The effect of catalyst weight was studied at 70 °C using phenol/1-dodecene molar ratio of 2 (Fig. 9). The conversion of dodecene was 47% with 1 wt.% catalyst (total weight of the reaction mixture), which increased to 67% with 3 wt.% catalyst. Further, increase in catalyst weight had no appreciable effect on conversion. Phenyldodecyl ether selectivity
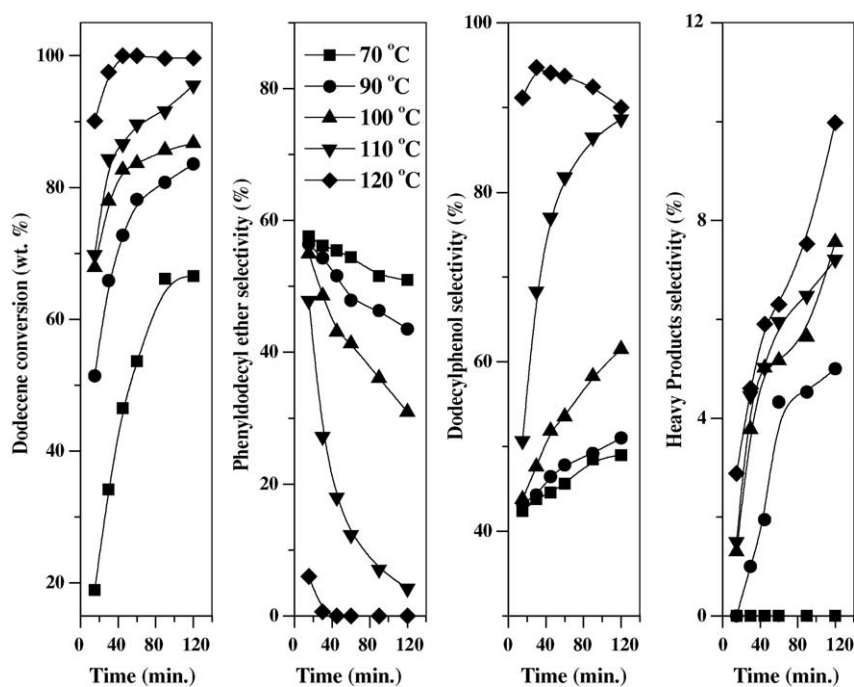

Fig. 7. Effect of reaction temperature on dodecene conversion and product selectivity. Conditions: total weight = 10 g, phenol/1-dodecene molar ratio = 2, catalyst weight = 3 wt.%.
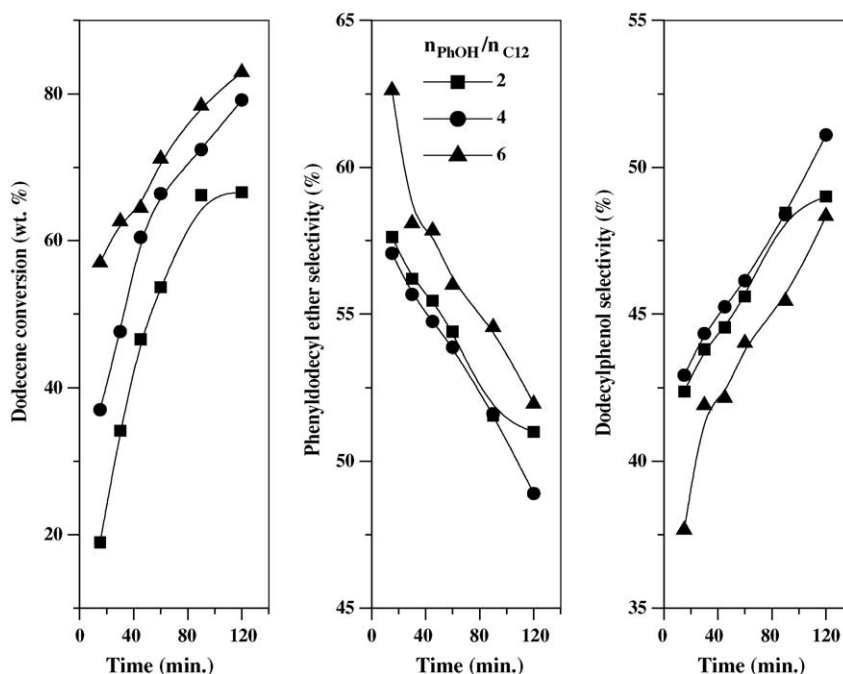
Fig. 8. Effect of phenol/1-dodecene molar ratio on dodecene conversion and product selectivity. Conditions: temperature = 70 °C, total weight = 10 g, catalyst weight = 3 wt.%.

was high with 1 wt.% catalyst and alkylphenol selectivity was low.

Additionally alkylation of phenol with other olefins like 1-decene and 1-octene was also carried out (Table 2). All olefins gave >99% olefin conversion and with 1-octene, formation of dialkylated product was observed.

3.2.6. Catalyst recycling

In order to study the recyclability of the catalyst, the reaction was studied at 120 °C with 3 wt.% catalyst using phenol/dodecene molar ratio 2 for 2 h (Fig. 10). Fresh catalyst showed >99% dodecene conversion in 2 h with 90% alkylphenol and 10% heavy products. For recycling, after
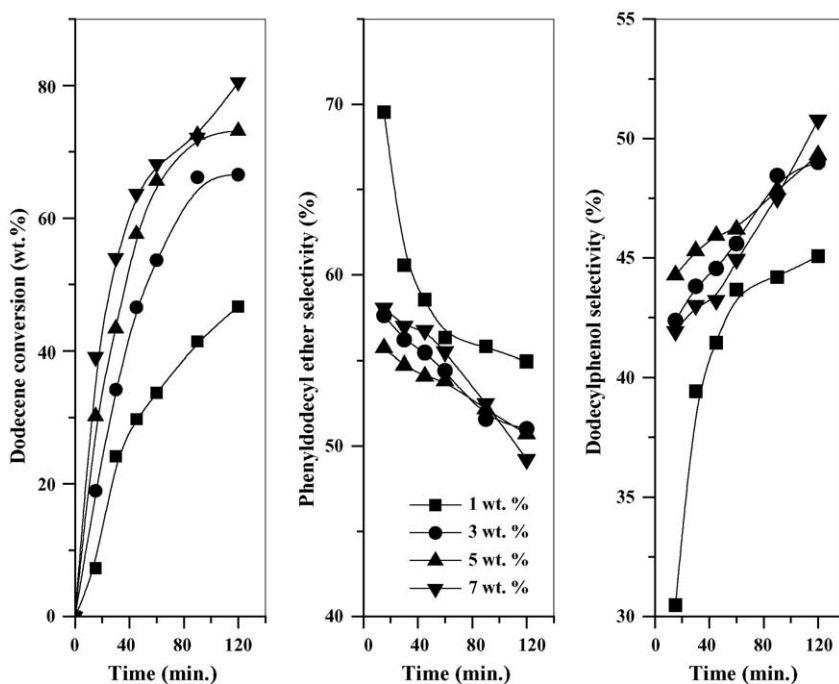

Fig. 9. Effect of catalyst weight on dodecene conversion and product selectivity. Conditions: temperature = 70 °C, total weight = 10 g, phenol/1-dodecene molar ratio = 2.
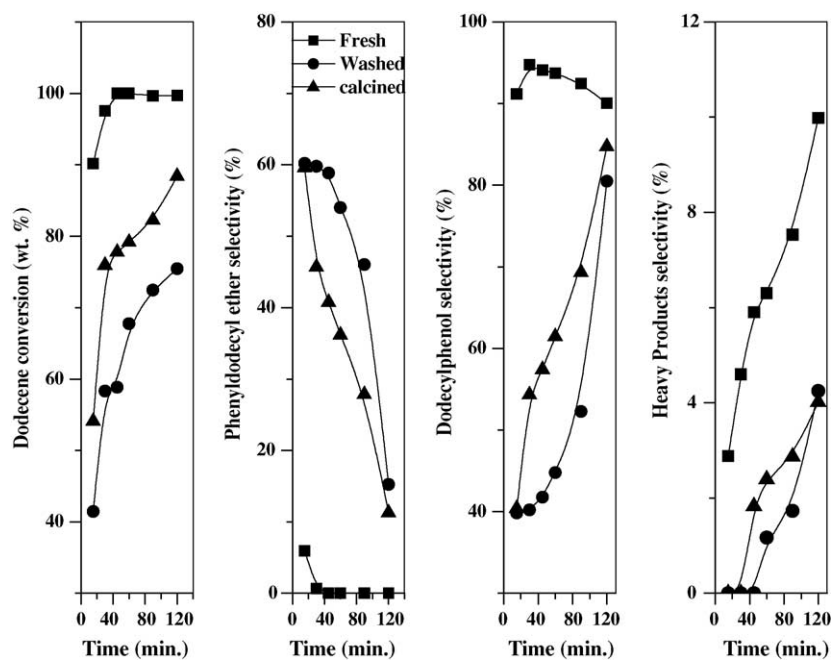
Fig. 10. Recycling of the catalyst 15 WZ-800 in alkylation of phenol with 1-dodecene. Conditions: temperature = 120 °C, total weight = 10 g, phenol/1-dodecene molar ratio = 2, catalyst weight = 3 wt.%.

first use, catalyst was separated by filtration, washed with methanol and dried at 100 °C for 5 h and rerun with fresh reaction mixture. The methanol washed catalyst showed 75% dodecene conversion with selectivity to phenyldodecyl ether 15%, dodecylphenol 81%, and heavy products 4% (2 h). However, after regeneration of the catalyst by calcination, dodecene conversion was found to be 88%, but selectivity to different products was similar to that of methanol washed

catalyst. The activity loss observed with the regenerated catalyst could be due to partial loss of acid sites of the catalyst during reaction/regeneration.

3.2.7. Comparison with zeolite Hβ and sulfated zirconia

The alkylation of phenol with 1-dodecene was studied using zeolite Hβ and sulfated zirconia (Fig. 11). The zeolite Hβ showed negligible activity, while activity of sulfated
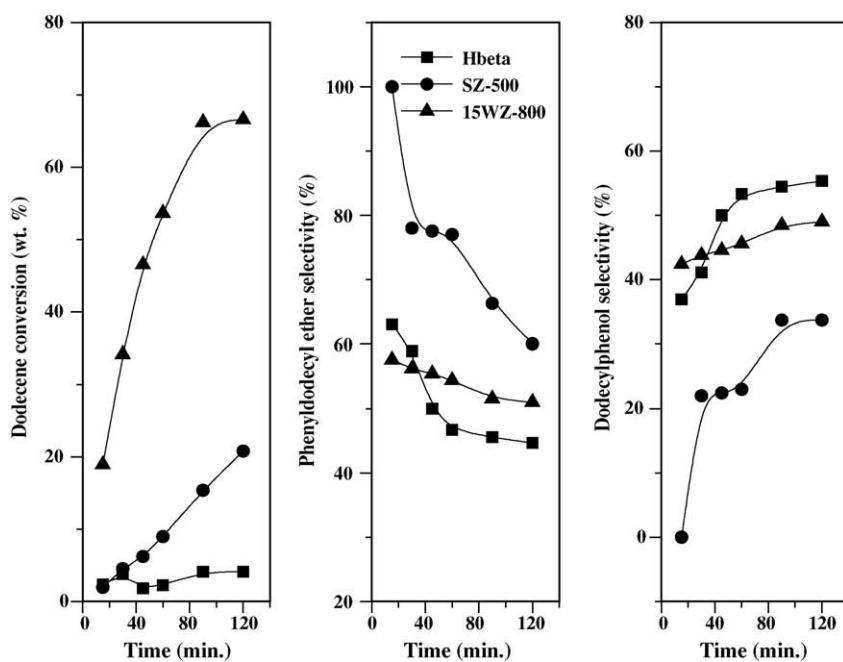

Fig. 11. Comparison of the catalytic activity of 15 WZ-800 with SZ-500 and Hβ zeolite. Conditions: temperature = 70 °C, total weight = 10 g, phenol/1-dodecene molar ratio = 2, catalyst weight = 3 wt.%.

Table 2
Alkylation of phenol with different 1-olefins catalyzed by 15 WZ-800

Alkene	Conversion (wt.%)	Selectivity (%)		
		Monoalkyl phenol	Dialkyl phenol	Heavy products
1-Octene	>99	79	21	0
1-Decene	>99	93	0	7
1-Dodecene	>99	90	0	10

Conditions: temperature = 120 °C, total weight = 10 g, phenol/1-olefin molar ratio = 2, catalyst weight = 3 wt.%.

zirconia was lower (21%) than that of 15 WZ-800 (67%). Sulfated zirconia initially gave only phenyldodecyl ether and with an increase in time its selectivity decreased and alkylphenol selectivity increased. The negligible activity of Hβ could be due to its pore structure, which prevents the diffusion of products, while the lower activity of sulfated zirconia and its higher selectivity to phenyl dodecyl ether could be due its lower acidity.

4. Conclusions

The liquid-phase alkylation of phenol with 1-dodecene has been studied in detail using WO_x/ZrO_2 catalysts and the catalytic activity has been compared with sulfated zirconia and Hβ zeolite. The catalyst 15 WZ-800 was found to be the most active and under the optimized reaction conditions of 120 °C, phenol/1-dodecene molar ratio 2 and time 2 h, dodecene conversion was >99% with 90% dodecylphenol selectivity. The activity of SZ-500 was lower than that of 15 WZ-800 and zeolite Hβ showed negligible activity. The catalyst 15 WZ-800 is also an efficient catalyst for alkylation of phenol with other long-chain olefins.

Acknowledgements

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