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Alkylation of benzene with α-olefins over zirconia supported 12-silicotungstic acid

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Abstract

Liquid phase alkylation of benzene to linear alkyl benzene (LAB) with α-olefins has been investigated with 12-silicotungstic acid supported on zirconia (STA/ZrO_2) as the catalyst. Among the catalysts, 15 wt.% STA/ZrO_2 calcined at 750 °C was found to be most active than others in the alkylation reaction. The total amount of acid sites of different STA loaded catalysts were estimated by TPD of NH_3 and 15 wt.% STA/ZrO_2 calcined at 750 °C was found to have the highest acidity and more active in the reaction. The optimization of reaction conditions of alkylation of benzene with 1-dodecene was performed with 15 wt.% STA/ZrO_2 calcined at 750 °C by varying catalyst concentration (1–5 wt.% of reaction mixture); temperature, 373–423 K and benzene:1-dodecene (1-dd) molar ratio, 5–15 in a Parr autoclave under N_2 pressure. Under the optimized reaction conditions, conversion of 1-dodecene (50.8%) gave high selectivity to 2-phenyl dodecane (47.1%) and the remaining 3-, 4-, 5- and 6-phenyldodecanes in 4 h. The reaction was found to be heterogeneously catalyzed and no contribution from homogeneous (leached) STA into the reaction medium.

Keywords: Alkylation; Benzene; 12-Silicotungstic acid; LAB; Zirconia; 1-Dodecene

1. Introduction

Linear alkyl benzenes (LABs) are important intermediates for synthetic detergents and these are traditionally manufactured in presence of aluminum trichloride or hydrofluoric acid catalysts. Because of the hazardous nature of conventional systems, there is a need to develop solid acid catalysts to replace the existing production methods. Solid acid catalysts such as zeolites [1–7], clays [8,9], heteropoly acids [10–14], fluorided silica-alumina [15], ionic liquids [16–18], H-ZSM-5, H-ZSM-12, H-Y [19–21], La-doped Y zeolite [22] and high silica mordenite (HSM) [23] have been widely investigated for the above transformations. Immobilized $AlCl_3$ over MCM-41 has been used for benzene alkylation with 1-olefins [24]. Already UOP/Petresa has industrialized a process with aluminum–magnesium silicate catalyst for alkylation of benzene with α-olefins [25,26]. A new catalytic distillation technology for benzene alkylation with α-olefins with suspended catalytic distillation (SCD) column has been developed [27]. Recently, supported tungstophosphoric acid catalyst was used for synthesizing LAB with high activities and with high selectivities to 2-LAB [28,29].

The present work deals with the alkylation of benzene with 1-dodecene using zirconia supported silicotungstic acid as the catalyst. The reaction was carried out with an aim to maximize 1-dodecene conversion together with the selectivity to 2-phenyldodecane as compared to other isomers like 3-, 4-, (5 + 6)-linear alkyl benzene. The influence of STA loading and catalyst calcination temperature on 1-dodecene conversion was studied. The catalyst with highest activity was used to study various reaction parameters such as temperature, molar ratio and catalyst weight. The catalyst regeneration and heterogeneity of reaction were also examined in the above reaction.

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2. Experimental

2.1. Materials

Zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) and ammonia (25%) were procured from S.D. Fine Chemicals Ltd., Mumbai. Benzene and 1-dodecene were obtained from Merck (India) Ltd. and Aldrich, respectively. Silicotungstic acid ($H_4SiW_{12}O_{40} \cdot xH_2O$) was purchased from Aldrich. All the chemicals were research grade and used as received without further purification in the catalyst preparation and alkylation experiments. Zeolites with (SiO_2/Al_2O_3 ratio), H-beta (30), H-ZSM-5 (60) and H-Y (13.5) recovered by calcining NH_4-Y were obtained from Catalysis Pilot Plant (CPP-NCL, Pune). H-Mordenite (20) was obtained from PQ Zeolites BV, Netherlands. All catalysts used in the reactions were in the powder form and were activated prior to their use in the reaction.

2.2. Preparation of STA/ZrO_2 catalysts

The catalysts were prepared by impregnation method using zirconium oxyhydroxide as the support by following our earlier reported procedure [30]. After impregnation, catalysts were dried and calcined in air at 750 °C. Catalysts with different STA loading 5–25 wt.% were prepared and calcined at 750 °C. STA/ZrO_2 (15 wt.%) was prepared and calcined at different calcination temperatures. Similarly, 15 wt.% STA/SiO_2 was prepared as above using silica gel and calcined at 750 °C. Silica gel support was prepared by known procedure [31].

2.3. Characterization

X-ray powder diffraction of the samples were carried out with Cu Kα radiation (Rigaku model D/MAXIII VC, Japan, $\lambda = 1.5418$ Å). The total amount of acid sites present on the catalysts with different TPA loadings were measured by TPD of ammonia. The acidity of the catalysts were measured by temperature programmed desorption of NH_3 (NH_3-TPD) using micromeritics AutoChem-2910 instrument. It was carried out after ∼0.5 g of the catalyst sample was dehydrated at 600 °C in He (30 $cm^3 min^{-1}$) for 1 h. The temperature was decreased to 100 °C and NH_3 was adsorbed by exposing samples treated in this manner to a stream containing 10% NH_3 in He for 1 h at 100 °C. It was then flushed with He for another 1 h to remove physisorbed NH_3. The desorption of NH_3 was carried out in He flow (30 $cm^3 min^{-1}$) by increasing the temperature to 600 °C at 10 °C min^{-1} measuring NH_3 desorption using TCD detector.

2.4. Aromatic alkylation

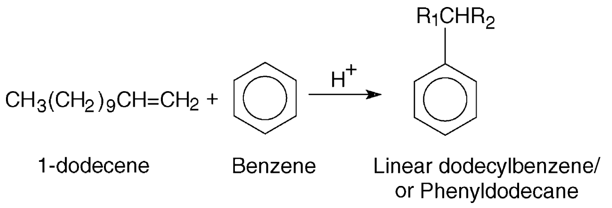
Experiments on alkylation of benzene were conducted in a 50 ml Parr autoclave under nitrogen pressure. The catalysts were activated at 500 °C for 4 h and cooled to room temperature prior to their use in the reaction. In a typical run, a weighted amount of 15 wt.% STA/ZrO_2 mixed with known amount of benzene and 1-dodecene was placed in the reactor. The reactor was pressurized with nitrogen (6–7 bar) and heated to the desired temperature with stirring at 500 rpm. After a fixed interval of time, the reactor was cooled to room temperature and a sample of the reaction mixture was withdrawn and centrifuged to get a clear solution and analyzed for products. The products of alkylation of benzene were analyzed by Shimadzu 14B gas chromatograph fitted with a SE-52 capillary column coupled with FID. Since, benzene was in excess, conversions were estimated based on the limiting alkylating reagent. The products were also identified by GC–MS analysis.

3. Results and discussion

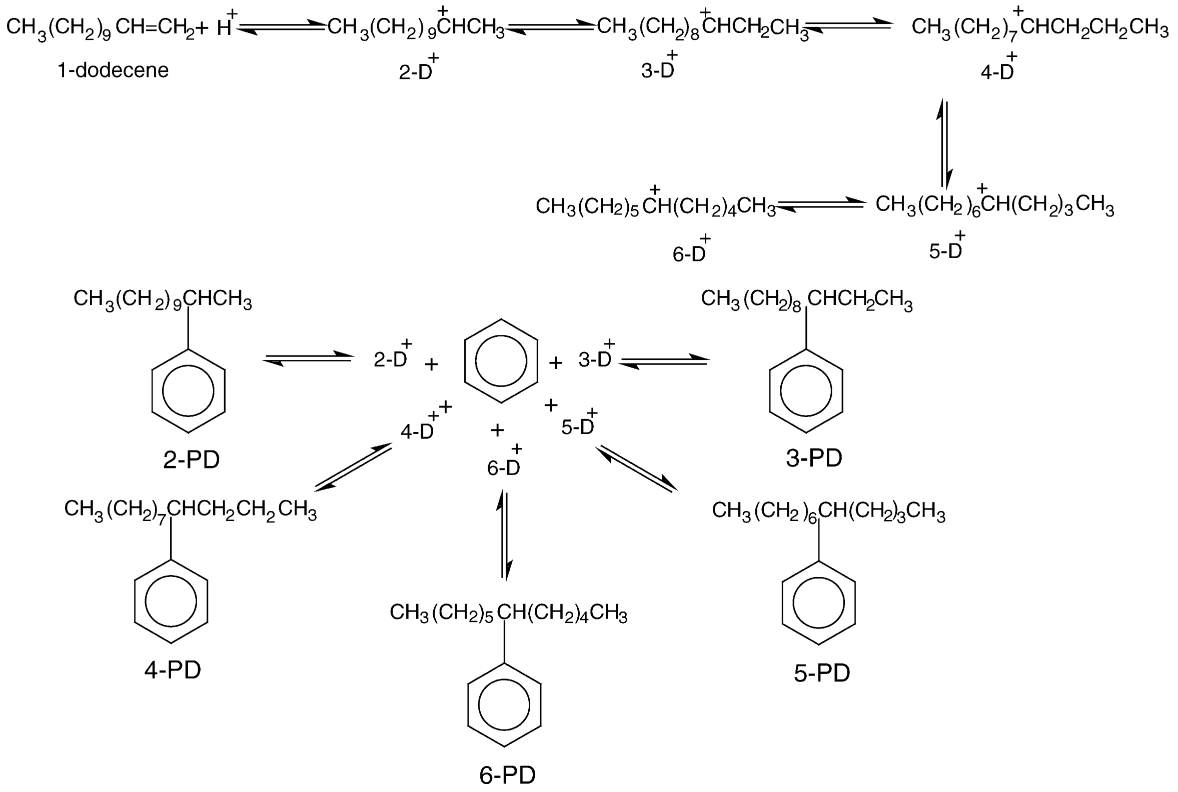
Alkylation of benzene with 1-dodecene catalyzed by 15 wt.% STA/ZrO_2 calcined at 750 °C under optimized reaction conditions gave 2-, 3-, 4- and (5 + 6)-phenyldodecane as shown in the Scheme 1. The formation of these isomers of phenyl dodecane are likely by the electrophilic substitution of cabenium ion, which is formed upon chemisorption of 1-dodecene on the catalyst surface as shown in Scheme 2.

3.1. Catalysts characterization

Wide angle XRD pattern for different STA (%) loadings over zirconia and calcined at 750 °C is shown in Fig. 1(A). Zirconia calcined at 750 °C mainly shows monoclinic form with small amount of tetragonal form. As (%) loading of STA increases, it shows increase in tetragonal phase, while 15 wt.% STA is showing fully tetragonal form of zirconia. This is due to monolayer coverage of STA over zirconia. But on further increase in STA loading, it shows monoclinic along with tetragonal phase and WO_3 crystallites due to the decomposition of STA (Keggin unit). Fig. 1(B) XRD pattern shows the effect of different calcination temperatures over 15 wt.% STA/ZrO_2. At calcination temperature of 750 °C, it shows fully tetragonal form of zirconia and on further increase in temperature WO_3 crystallites are observed. Acidity measurement by TPD of ammonia is shown in Figs. 2 and 3 along with catalytic activity. From Fig. 2, it is seen that with increase in STA loading up to 15 wt.%, it shows increase in acidity and so catalytic activity. But on further increase in STA loading,



Scheme 1. Alkylation of benzene with 1-dodecene.



Scheme 2. Mechanism of formation of linear phenyldodecanes (PD).

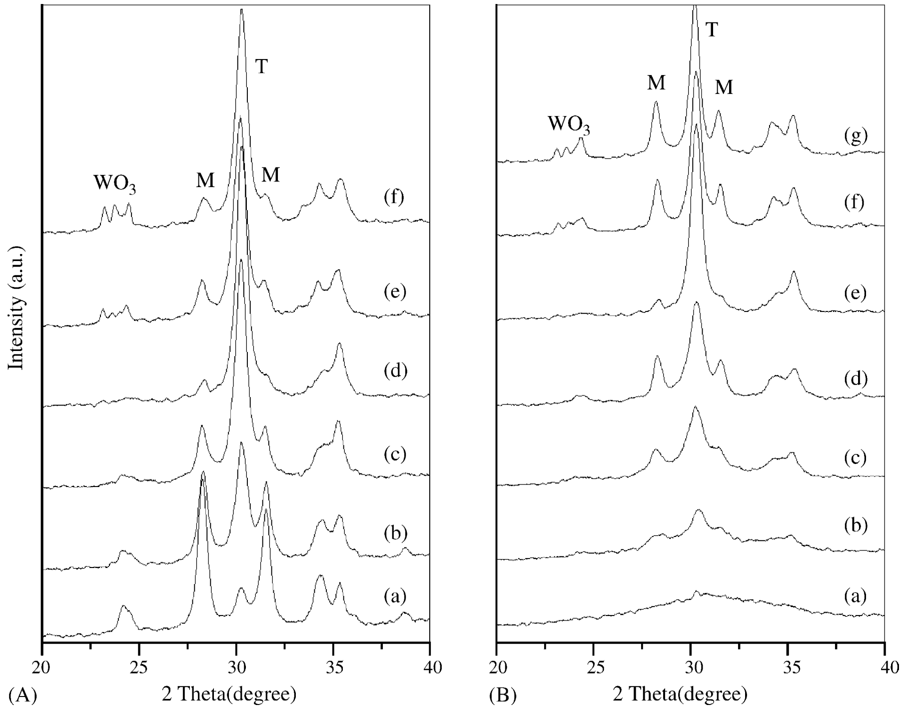


Fig. 1. XRD patterns of (A) ZrO_2 (a), 5 wt.% (b), 10 wt.% (c), 15 wt.% (d), 20 wt.% (e), and 25 wt.% (f) catalysts calcined at 750 °C and (B) 15 wt.% catalyst calcined at (a) 350 °C, (b) 450 °C, (c) 550 °C, (d) 650 °C, (e) 750 °C, (f) 800 °C, and (g) 850 °C.

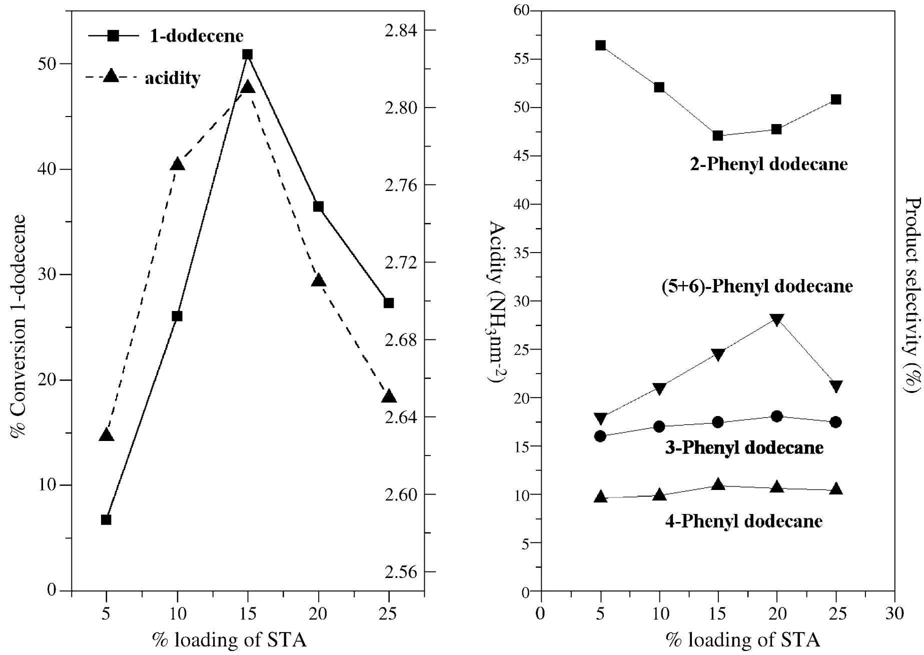


Fig. 2. Effect of STA loading and acidity on 1-dodecene conversion and product selectivity. Conditions: temperature = 130 °C, benzene/1-dodecene molar ratio = 10, catalyst weight = 0.6 g (3 wt.% of total reaction mixture), N_2 pressure = 6–7 bar, time = 4 h.

the acidity decreases due to decomposition of STA into WO_3 crystallites. As calcination temperature of 15 wt.% STA/ZrO_2 increases up to 750 °C, it shows high acidity with maximum activity due to monolayer coverage of STA over zirconia. But on exceeding calcination temperature above 750 °C, it shows decrease in acidity due to the formation of WO_3 crystallites.

3.2. Activities of different catalysts in alkylation of benzene by 1-dodecene

The catalytic activities of different catalysts such as H-beta, H-Y, H-ZSM-5, H-Mordenite, neat STA, 15 wt.% STA/SiO_2, and 15 wt.% STA/ZrO_2 calcined at 750 °C tested in the alkylation of benzene with 1-dodecene under identical

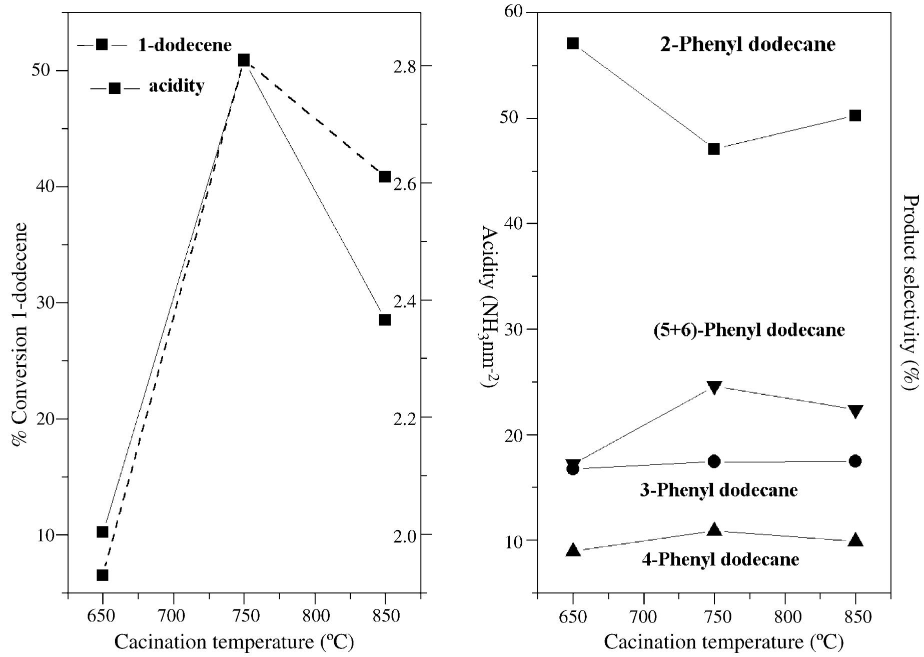


Fig. 3. Effect of calcination temperature and acidity on 1-dodecene conversion and product selectivity. Conditions: temperature = 130 °C, benzene/1-dodecene molar ratio = 10, catalyst weight = 0.6 g (3 wt.% of total reaction mixture), N_2 pressure = 6–7 bar, time = 4 h.

Table 1
Activities of different catalysts in alkylation of benzene with 1-dodecene

Catalyst	1-Dodecene conversion (wt.%)	Acidity (mmol/g)	%Selectivity			
			2-PD	3-PD	4-PD	(5 + 6)-PD
Neat STA	0.7	–	75.9	15.3	4.5	4.3
15% STA/ZrO_2^{750}	50.8	0.25	47.1	17.4	10.9	24.6
15% STA/SiO_2^{750}	6.6	Nil	59.2	16.2	8.5	16.1
H-β (30)	39.0	0.94	62.4	19.6	7.1	10.9
H-Y (13.5)	44.9	2.25	36.4	22.1	14.4	27.1
H-Mordenite (20)	4.7	0.72	89.5	10.5	–	–
H-ZSM-5 (60)	0.1	0.82	100	–	–	–

Reaction conditions: benzene:1-dd = 10:1 (molar ratio), pressure = 6–7 bar, amount of catalyst = 600 mg (3 wt.% of total reaction mixture), reaction time = 4 h. In bracket, (Si/Al) ratio of respective zeolites are given. PD: phenyldodecane.

reaction conditions and the results are summarized in Table 1. It is seen from the results that STA (neat) gave the poorest conversion, which is due to its low surface area. It is also observed that 15 wt.% STA/SiO_2 calcined at 750 °C shows very less catalytic activity in the reaction, since it has no acidity required for acid catalyzed reactions. The absence of acidity in 15 wt.% STA/SiO_2 calcined at 750 °C confirmed that STA decomposed on SiO_2 support and lost its acidity. Among the zeolite catalysts, H-Y is more active than others due to its highest acidity with large pores gave higher conversion of 1-dodecene followed by H-beta (strong and medium acid sites). Similarly, poorest activity of H-ZSM-5 might be explained on the basis of its smaller pore size compared with the larger size of the products. While, H-Mordenites has one-dimensional pore with elliptical channels, 6.5 × 7.0 also has the low activity. Therefore, we chose 15 wt.% STA/ZrO_2 calcined at 750 °C as the catalyst for further investigations on its catalytic performance in the benzene alkylation with 1-dodecene.

3.3. Effect of STA loading on ZrO_2 in the alkylation of benzene by 1-dodecene

Alkylation experiments were conducted using different STA loaded (5–25 wt.%) catalysts to know the effect on the conversion of 1-dodecene and the results are shown in Fig. 2. It is seen that conversion of 1-dodecene increased with increase in STA loading up to 15 wt.% and decreased with further increase in loading. As shown in Fig. 2, 15 wt.% catalyst is more acidic than others, hence it gave highest 1-dodecene conversion (50.8%) under the optimized reaction conditions. From the results presented in Fig. 2, it is evident that the selectivity for 2-phenyl dodecane is higher than the other isomers of LAB.

3.4. Effect of calcination temperature in alkylation of benzene by 1-dodecene

For studying the effect of calcination temperatures on 15 wt.% STA/ZrO_2 catalyst, alkylation of benzene by 1-dodecene was conducted and the results are shown in Fig. 3. From the results, it is seen that the conversion of 1-dodecene increases up to 750 °C calcination temperature and then on further increase in calcination temperature, the conversion of 1-dodecene decreased. This observation also supports the fact that 15 wt.% STA/ZrO_2 calcined at 750 °C has the maximum concentration of acid sites, where STA forms a monolayer coverage over the support. Hence, catalyst calcined at 750 °C was chosen for further study.

3.5. Effect of catalyst concentration in alkylation of benzene by 1-dodecene

To know the effect of 15 wt.% STA/ZrO_2 catalyst concentrations on the conversion of 1-dodecene and the product distribution in the alkylation of benzene, the reaction was conducted by changing the catalyst concentration in the range of 1–5 wt.% of total reaction mixture (20 g), keeping constant molar ratio of benzene:1-dodecene (1-dd) as 10, 403 K and 4 h. The results are shown in Fig. 4 as conversion of 1-dodecene as a function of catalyst concentration. It is seen from the Fig. 4 that the conversion of 1-dodecene increased from 7.4 to 80% linearly in 4 h, giving highest selectivity for 2-phenyl dodecane.

3.6. Effect of reaction temperature in alkylation of benzene by 1-dodecene

The alkylation of benzene was carried out in the temperature range 100–150 °C to know the effect of temperature on the conversion of 1-dodecene and the product selectivities (Fig. 5). The effect of temperature on conversion of 1-dodecene along with product selectivities for all LAB isomers are shown in Fig. 5 along with the reaction conditions. It is seen from the Fig. 5 that the conversion of 1-dodecene is increased from 4.3 to 82.2% with increase in temperature from 100 to 150 °C. The optimum conversion of 1-dodecene (50.8%) was obtained at 130 °C with product selectivites 2-LAB (47.1%), 3-LAB (17.4%), 4-LAB (10.9%) and (5 + 6)-LAB (24.6%), respectively. Activation energy evaluated from the graph—ln rate versus 1/T was found to be

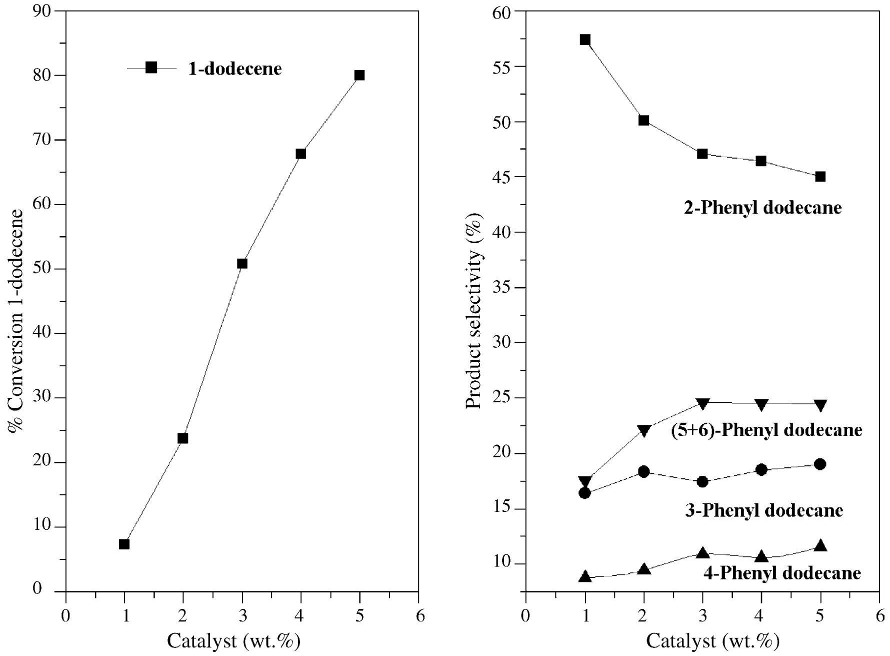


Fig. 4. Effect of catalyst weight on 1-dodecene conversion and product selectivity. Conditions: temperature = 130 °C, benzene/1-dodecene molar ratio = 10, N_2 pressure = 6–7 bar, time = 4 h.

34.7 kcal mol^{-1}. Interestingly, the above reaction conducted in a pot-open atmospheric system gave higher rates at reflux temperature than the closed (autoclave) system in presence of nitrogen atmosphere at higher temperatures. The reasons for lower rates observed in a closed system needs further investigation.

3.7. Effect of molar ratio in the alkylation of benzene by 1-dodecene

The effect of benzene:1-dodecene molar ratio on the conversion of 1-dodecene and product distribution are presented in Fig. 6. The mole ratio of benzene:1-dd was changed from

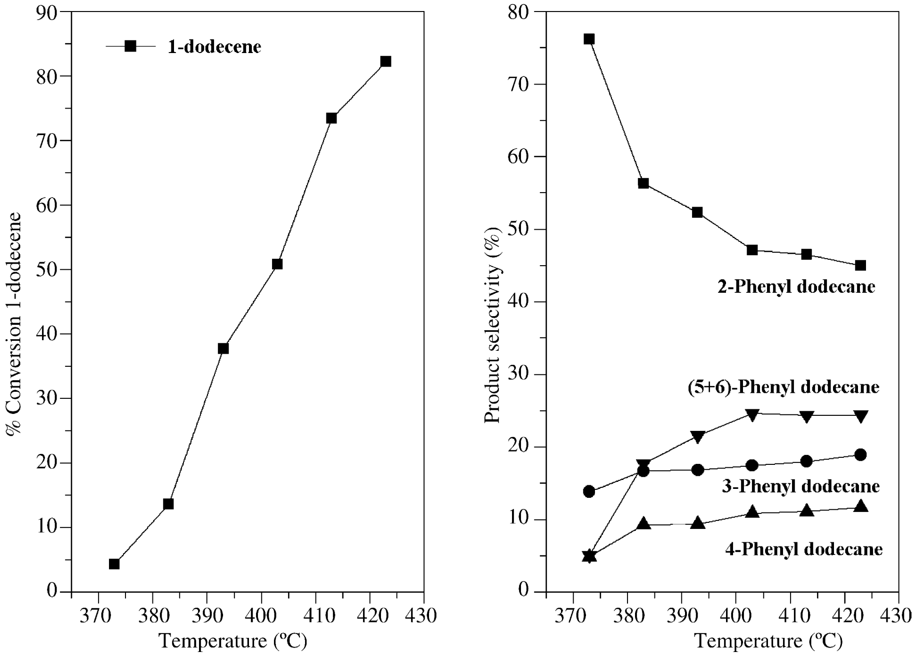


Fig. 5. Effect of temperature on 1-dodecene conversion and product selectivity. Conditions: benzene/1-dodecene molar ratio = 10, catalyst weight = 0.6 g (3 wt.% of total reaction mixture), N_2 pressure = 6–7 bar, time = 4 h.

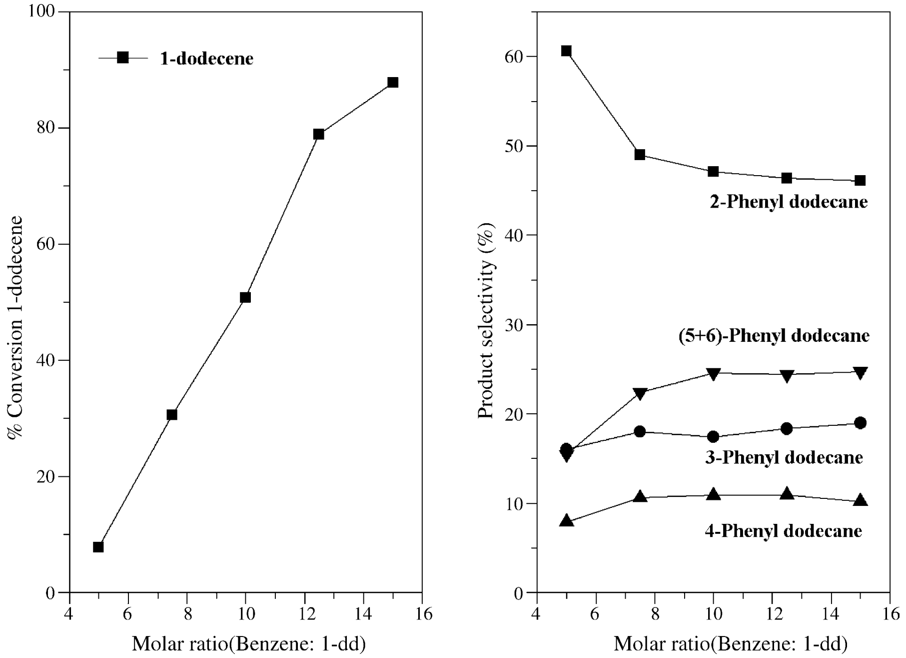


Fig. 6. Effect of molar ratio on 1-dodecene conversion and product selectivity. Conditions: temperature = 130 °C, catalyst weight = 0.6 g (3 wt.% of total reaction mixture), N_2 pressure = 6–7 bar, time = 4 h.

5 to 15, keeping other conditions the same. As benzene:1-dd molar ratio is increased from 5 to 15, conversion of 1-dd increased linearly from 7.8 to 87.8 with high selectivity for 2-phenyl dodecane.

3.8. Time on stream study

In order to study the effect of time on stream, alkylation reaction was studied as a function of time under optimized conditions and the results are shown in Fig. 7. Conversion of 1-dodecene was almost linearly increased with increase in time from 23.6 to 76.9%, while 2-phenyl dodecane has the highest selectivity.

3.9. Alkylation of benzene with other olefins

To investigate the effect of chain length of α-olefins, the benzene alkylation was carried out with 1-octene and 1-

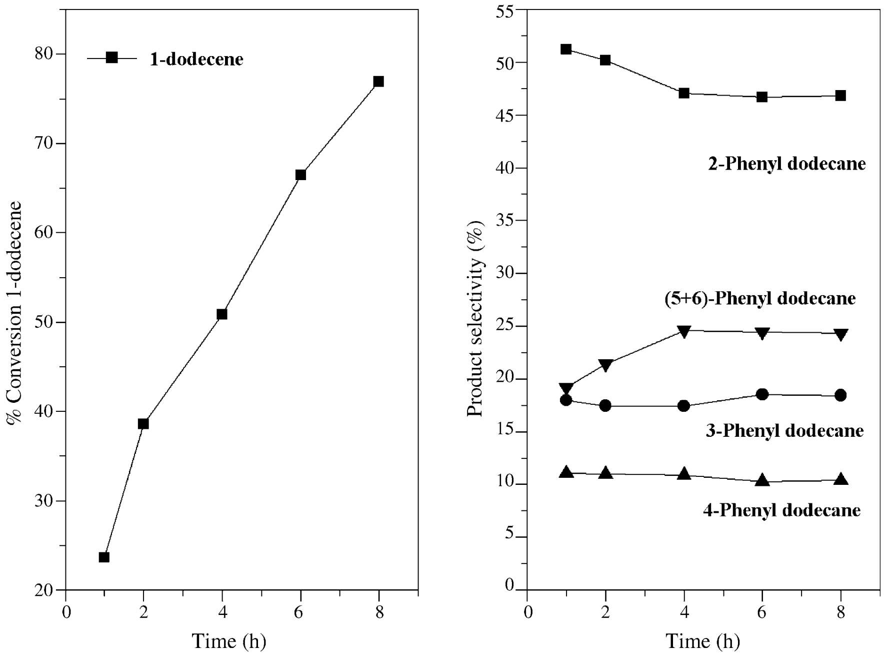


Fig. 7. Effect of reaction time on 1-dodecene conversion and product selectivity. Conditions: temperature = 130 °C, benzene/1-dodecene molar ratio = 10, catalyst weight = 0.6 g (3 wt.% of total reaction mixture), N_2 pressure = 6–7 bar.

Table 2
Alkylation of benzene by different 1-olefines with 15 wt.% STA/ZrO2 calcined at 750 °C

Alkylating agent	1-Olefin conversion (wt.%)	%Selectivity			
		2-LAB	3-LAB	4-LAB	(5 + 6)-LAB
1-Dodecene	50.8	47.1	17.4	10.9	24.6
1-Decene	52.2	57.9	18.9	23.2 (4- and 5-)	–
1-Octene	54.5	63.6	21.9	14.5	–

Reaction conditions: benzene:1-dd = 10:1 (molar ratio), N_2 pressure = 6–7 bar, amount of catalyst = 600 mg (3 wt.% of total reaction mixture), temperature = 130 °C, reaction time = 4 h. LAB: linear alkyl benzene.

decene under similar optimized reaction conditions using 15% STA/ZrO_2 calcined at 750 °C. It was found that the conversion of 1-olefins in general was decreased with increase in chain length of α-olefin as presented in Table 2. Also from results, it is seen that with increase in chain length, selectivity for respective 2-LAB products were decreased.

3.10. Leaching and recyclability of the catalyst

In order to check the leaching of STA into the reaction mixture and an absence of homogeneous reaction, alkylation of benzene with 1-dodecene was carried out for 2 h under optimized reaction conditions using fresh 15% STA/ZrO_2 calcined at 750 °C. The reaction was stopped and catalyst was separated by filteration and then same reaction mixture was stirred further for 2 h under same reaction conditions. It was found that in the absence of the catalyst, there was no further increase in the conversion of 1-dodecene, which indicated the absence of leaching of STA into the reaction mixture. This observation confirmed that the reaction was catalyzed heterogeneously. In addition to this, leaching of STA (dissolution of Si or W) into the filtrate was tested by inductively coupled plasma-optical emission spectroscopy (ICP-OES). This showed that the filtrate did not contain Si or W and were completely absent in solution, which confirmed that alkylation reaction occurred heterogeneously by surface mechanism.

For testing catalytic activity of regenerated catalyst, the catalyst used in the first cycle of the reaction was separated by filteration, washed two to three times with 1,2-dichloromethane and then dried in an oven for overnight at 100 °C. Then catalyst is activated at 500 °C for 4 h in an airflow. This activated catalyst is further used for alkylation of benzene with dodecene under optimized reaction conditions. Same procedure is repeated for second cycle also and results of this study are presented in Table 3. From the result, it is concluded that after second cycle also there is no considerable decrease in the catalytic activity and product selectivities. Hence, the catalyst is recyclable and could be used in many catalytic cycles alkylation reactions.

Table 3
Recyclability of catalyst

Cycle	1-Dodecene conversion (wt.%)	%Selectivity			
		2-PD	3-PD	4-PD	(5 + 6)-PD
Fresh	50.8	47.1	17.4	10.9	24.6
First run	50.7	47.8	17.3	10.7	24.2
Second run	48.7	48.0	17.3	10.7	24.0

Reaction conditions: benzene:1-dd = 10:1 (molar ratio), pressure = 6–7 bar, catalyst = 15 wt.% STA/ZrO_2^{750}, amount of catalyst = 600 mg (3 wt.% of total reaction mixture), time = 4 h, temperature = 130 °C. PD: phenyldodecane.

4. Conclusions

Alkylation of benzene with 1-dodecene was carried out over 15 wt.% STA/ZrO_2 catalyst calcined at 750 °C in liquid phase conditions under N_2 atmosphere. The catalyst with 15 wt.% loading showed highest catalytic activity at 130 °C with benzene:1-dd molar ratio 10 and 3 wt.% catalyst concentration (of the total reaction mixture). Under the optimized reaction conditions, STA/ZrO_2 showed good catalytic activity with a maximum conversion of 1-dodecene (50.8%) and shape selectivity to 2-phenyl dodecane (47.1%) as compared with other isomers like 3-, 4-, 5- and 6-phenyl dodecane at 130 °C. The above catalyst was recyclable, cost effective and environmental friendly and could be used in similar reactions.

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