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Paper Authors

**P.Geetha, Anil Kumar Turaka, Subbarao. K, B.N. Srinivas, P. Ramesh Babu**



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## Chromia supported on Activated carbon prepared from Rice husk: Activity study on Dehydration of 1, 4-butanediol to Tetrahydrofuran and 1-phenylethanol to Styrene

P.Geetha<sup>\*1</sup>, Anil Kumar Turaka<sup>2</sup>, Subbarao. K<sup>3</sup>, B.N. Srinivas<sup>4</sup>, P. Ramesh Babu<sup>5</sup>

<sup>\*1</sup>Department of Chemistry, Ramachandra College of Engineering, Eluru, A.P-534007

<sup>2</sup>Department of Chemistry, Krishna University, Machilipatanam, A.P

<sup>3</sup> Department of Chemistry, Malla Reddy Engineering College (A), Secunderbad, Telangana-500100

<sup>4</sup>Department of Chemistry, UshaRama College of Engineering & Technology, Telaprolu, A.P

<sup>5</sup>Department of Physics, Gokaraju Rangaraju Institute of Engineering & Technology, Hyderabad, Telangana-500090.

[geethapillutla44@gmail.com](mailto:geethapillutla44@gmail.com)

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### Abstract:

The main objective of this study is preparation of Activated carbon (AC) from Rice husk. This AC is used to support for preparation of catalyst of 35wt% Cr/RHAC and catalyst is characterization by X-ray diffraction (XRD), surface area (SA), pore size distribution (PSD) and Thermo gravimetric analysis (TGA). Dehydration of 1- phenylethanol to styrene over 30wt% Cr/RHAC catalyst, temperature range 246°C to 267°C in the vapor phase reaction. The conversion of 1- phenylethanol to styrene is 95% due to well dispersion of Chromia on RHAC support small particle size of Chromia and more acidic strength. AC prepared from rice husk show good SA 312 m<sup>2</sup>g<sup>-1</sup> and PSD 3.13nm. So that catalyst shows very good activity and selectivity towards the desired product. The activity of catalyst remains same during the time on stream due to high porosity and acidity.

**Keywords:** 35wt% Cr/RHAC catalyst, Dehydration, XRD, SA, PSD, TGA.

### 1. Introduction:

Paddy is the main source to get food in India, annually almost produce 281.37 million tonnes in 2018-19 [1]. It is one of the renewable resource and biomass which having rich in silica and Activated carbon. The physical and surface chemical properties of activated carbons can be modified by several different heat treatments and impregnation

procedures [2-4]. Activated carbons (AC) are made from materials rich in carbon through carbonization and an activation process. A porous structure and its adsorption properties can be obtained in carbonaceous materials via either chemical or physical [5] activation. Physical activation involves pyrolysis of the source material at 800°C -1000°C to produce charcoal. This is then followed by activation

using steam, carbon dioxide (CO<sub>2</sub>) or oxygen (O<sub>2</sub>). Chemical activation involves the impregnation of the precursor material with a chemical activating agent followed by activation at temperatures of 400°C-700°C under nitrogen atmosphere [6]. Zinc chloride (ZnCl<sub>2</sub>), potassium hydroxide (KOH) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) are widely used as chemical activating agents.

Reaction in vapor phase has been carried out over solid acid catalysts like silica gel, alumina, alkali alumina, aluminum silicates and H-type synthetic zeolites and metal oxide catalysts such as titanium, thorium or aluminum oxide [7-10]. In general chromium based catalysts were used for the transformation of alkyl aromatic to aromatic ketones and acids in homogenous medium. However excess usage of chromium catalyst has adverse effect on environment due to the toxic nature of chromium [11]. Therefore, in recent years considerable attention has been paid for the use of chromium based heterogeneous catalysts for wide variety of organic transformations such as oxidation of aromatics, dehydrogenation, epo-oxidation of olefins and allylic oxidation reactions [12-13].

Present work dehydration of 1-phenylethanol to styrene over 35 wt% Cr/RHAC catalyst in vapor phases the temperature range 246°C to 267°C. The main reason for studying this catalyst system is to establish advantage of the porous structure of 35 wt% Cr/RHAC compared to the conventional catalyst. In addition, effect of temperature and time on stream studies was systematically investigated.

## 2. Materials and Methods:

### 2.1 Preparation of Activated carbon from Rice husk:

10 g of pyrolytic rice husk char were pretreated with 200 ml of HCl (1 M) to remove most of the impurities and to improve the purity of the silica. The char was introduced in a flask and the suspension was boiled for 3 h under reflux condenser and vigorous stirring. Then, the suspension was filtered and the solid was washed with distilled water until neutral pH. Finally the char recovered was dried for 15 h at 120 °C. The next step was to remove the silica with a 15 wt. % Na<sub>2</sub>CO<sub>3</sub> solution. The char and 200 ml of this solution were introduced in a flask and boiled for 4 h under reflux condenser. The suspension was filtered and the precipitate was washed with distilled water until the pH becomes neutral followed by drying at 120°C for 24 h. The precipitate is the resulting carbon material from which activated carbon materials can be prepared chemical activation process. Take 5 gr of activate carbon is impregnated with 30 wt. % of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and then heated at 250°C under air for 2 hr. Then the same sample is subjected to heating at 600°C under nitrogen atmosphere for activation. This is noted as RHAC.

### 2.2. Preparation of 35 wt% Cr/RHAC catalyst:

35 wt% Chromia on RHAC is prepared by wet impregnation method using requisite quantity of chromium nitrate monohydrate. The material was dried at 383 K overnight followed by calcinations in nitrogen flow of 70 ml/min at 873 K for 4 hours and is denoted as 35wt% Cr/RHAC [14-15].

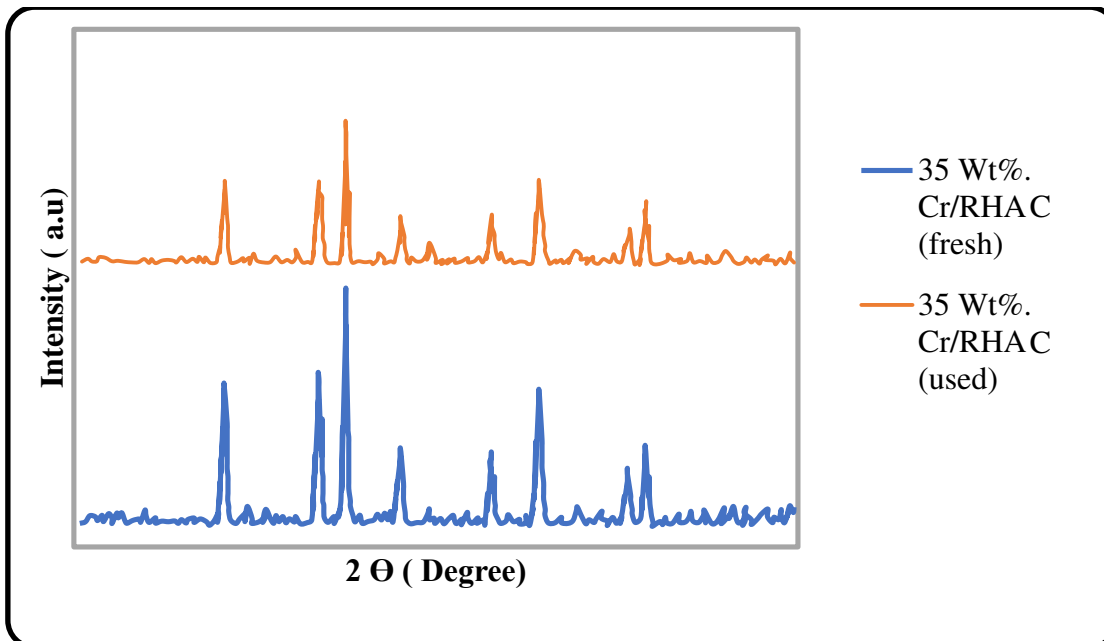
## 3. RESULTAS AND

## DISCUSSIONS

### 3.1 Pure RHAC and 35wt% Cr/RHAC XRD studies:

Fig: 1 shows the diffraction pattern of 35 wt% Cr/RHAC which witness well resolved diffraction peaks at  $2\theta = 24.30^\circ, 33.12^\circ, 36.20^\circ, 41.56^\circ, 49.34^\circ, 54.08^\circ, 63.14^\circ$  and  $65.04^\circ$  due to the presence of Rhombohedral

chromium oxide. Very small peaks present between  $30-40^\circ$  is attributed to the presence of Si-O-Si structures on the surface of the support material. There is no huge change in the crystalline of the pre-owned impetus. The arrangement of coke superficially impetus diffraction force might be decline.



**Fig: 1** X-ray patterns of 35wt% Cr/RHAC, a) fresh and b) used

### 3.2 N<sub>2</sub> adsorption – desorption isotherms:

The textural properties of Rice Husk Activated Carbon (RHAC) and 35wt% Cr/RHAC of new and utilized catalyst got from nitrogen adsorption-desorption isotherm are abridged in Table: 1, which shows surface territory and pore size distribution of 35wt% Cr/RHAC of new and utilized

catalyst. Pure RHAC have high explicit surface region ( $312\text{m}^2\text{g}^{-1}$ ) and pore volume ( $0.35\text{cm}^3\text{g}^{-1}$ ). Explicit surface area and pore volume of 35wt% Cr/RHAC catalyst ( $287.4\text{m}^2\text{g}^{-1}$  and  $0.29\text{cm}^3\text{g}^{-1}$  individually) is diminished after response ( $271.2\text{m}^2\text{g}^{-1}$  and  $0.25\text{cm}^3\text{g}^{-1}$  separately) contrasted with Cr/RHAC because of pore blockage by Chromia.

Catalysts	Surface area <sup>a</sup> ( $\text{m}^2/\text{g}$ )	Average pore size <sup>b</sup> (nm)	Pore volume ( $\text{cm}^3/\text{g}$ )
Pure RHAC	312	3.12	0.35



35wt % Cr/RHAC (fresh)	287.4	3.09	0.29
35wt% Cr/RHAC (used)	271.2	2.92	0.25

<sup>a</sup> Surface area by BET method      <sup>b</sup> Average pore size

Table: 1 Textural properties of Chromium catalysts

### 3.3 Thermo Gravimetric Analysis:

Thermo gravimetric analysis of pure RHA and 35wt% Cr/RHAC are depicted in Fig: 2 Pure RHAC sample witnesses a weight loss in the temperature range from 323 – 373K due to the removal of crystalline water molecule and another weight

loss in the temperature range from 523 – 673K due to the elimination of volatile organic matter. In the TGA analysis of 35wt% Cr/RHAC, the weight reduction in the scope of 373-473 K is because of the disintegration of chromium nitrate prompting arrangement of Cr<sub>2</sub>O<sub>3</sub> on RHAC.

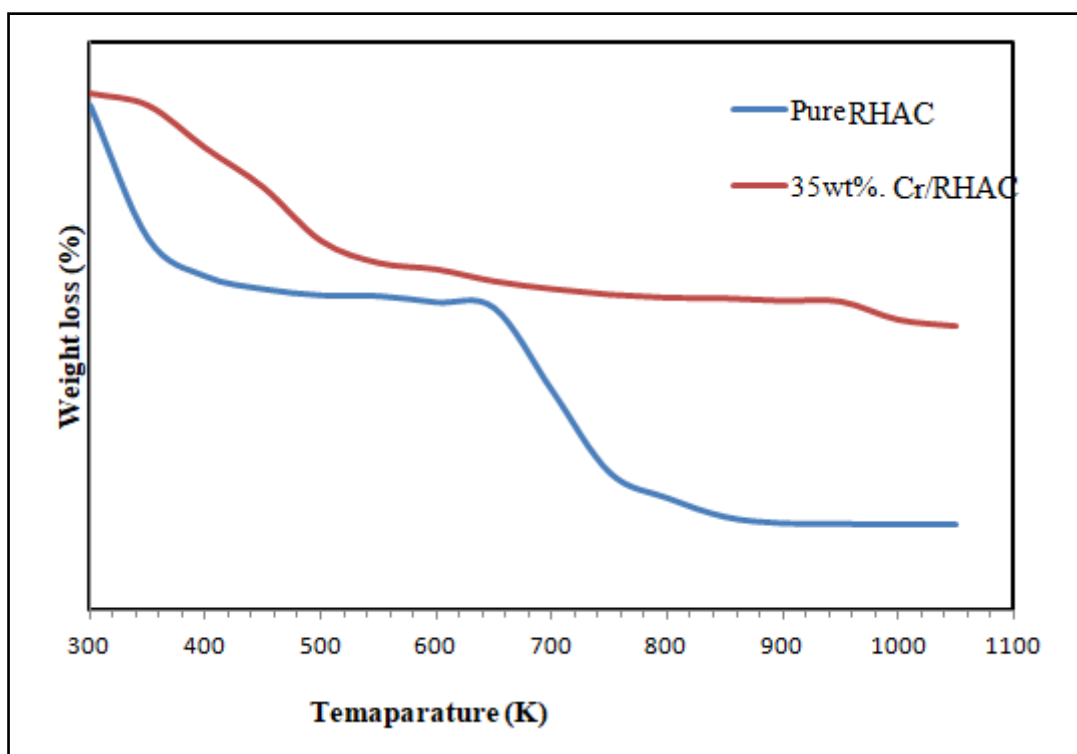


Fig. 2 Thermo gravimetric analysis of a) Pure RHAC b) 35wt% Cr/RHAC

### Catalysts

### 3.4 Catalytic Activity Study

Vapor phase dehydration of 1,4-butanediol and 1-phenylethanol was carried out in a fixed bed down flow reactor (10 mm id and 300 mm long glass reactor) using 1g 35wt%

Cr/RHAC catalyst at atmospheric pressure. Reaction temperature ranging from 540 to 565 K for 1, 4-butanediol and 520 to 540 K for 1-phenylethanol was maintained. The product samples were collected at

regular intervals of time in an ice cold trap and were analyzed by GC.

## 4 Activity Study of 35wt% Cr/RHAC Catalyst:

### 4.1 Dehydration of 1, 4-butanediol to Tetrahydrofuran:

Dehydration reaction of 1, 4-butanediol to Tetrahydrofuran over Cr/RHAC catalyst in the temperature kept up 540-564K. Where the transformation pace of 1, 4-butanediol to Tetrahydrofuran is 36% when 35wt% Cr/RHA is utilized as a catalyst. Table: 2 It is compared with earth metal oxides like Yb<sub>2</sub>O<sub>3</sub>,

CeO<sub>2</sub>, and ZrO<sub>2</sub> shows low transformation however most noteworthy selectivity [15-19]. 35wt% Cr/RHA has low transformation rate when contrasted and other uncommon earth metal oxide catalyst because of essence of lower acidic sites [20]. The time on stream concentrates more than 35 Wt. % Cr/RHA catalysts at 540 K. also; figure: 3 shows there are no loss of synergist action and selectivity of THF much following 10 hours of activity.

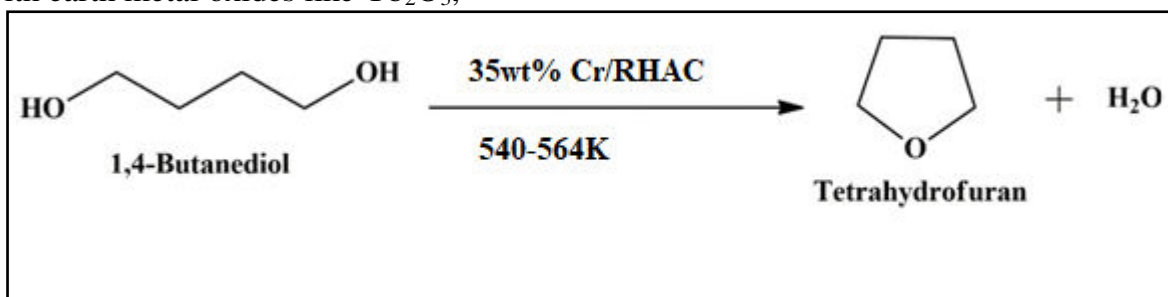


Fig. 3. Dehydration of 1, 4-butanediol to Tetrahydrofuran

Table: 2. Comparative study of 35 wt. % Cr-RHAC with literature

Catalyst	Te mp. (K)	Con v. %	Selecti vity of THF
10 wt.% La/ZrO <sub>2</sub>	598	94.4	65.9
CeO <sub>2</sub>	698	73.4	7.4
ZrO <sub>2</sub>	623	86.4	44.9
Na-ZrO <sub>2</sub>	648	90.1	28.0
Yb <sub>2</sub> O <sub>3</sub>	648	40.3	2.7
35 wt. % Cr/RHA C	540	36.0	100

reported Catalyst in dehydration over various oxide catalysts.

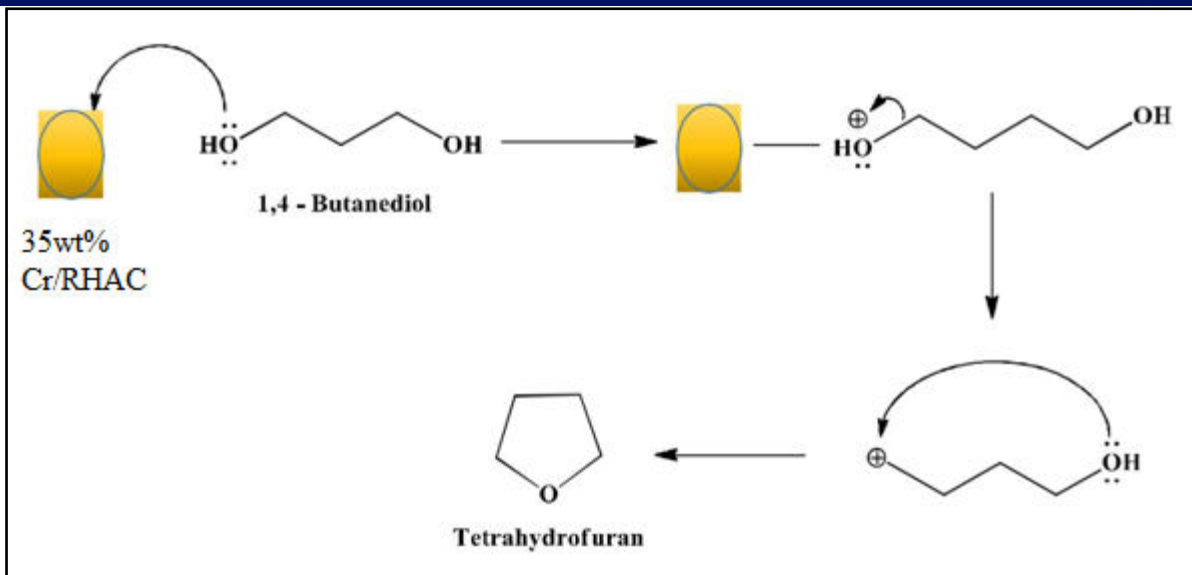


Fig: 4. Plausible mechanism of 1, 4 butanediol to THF.

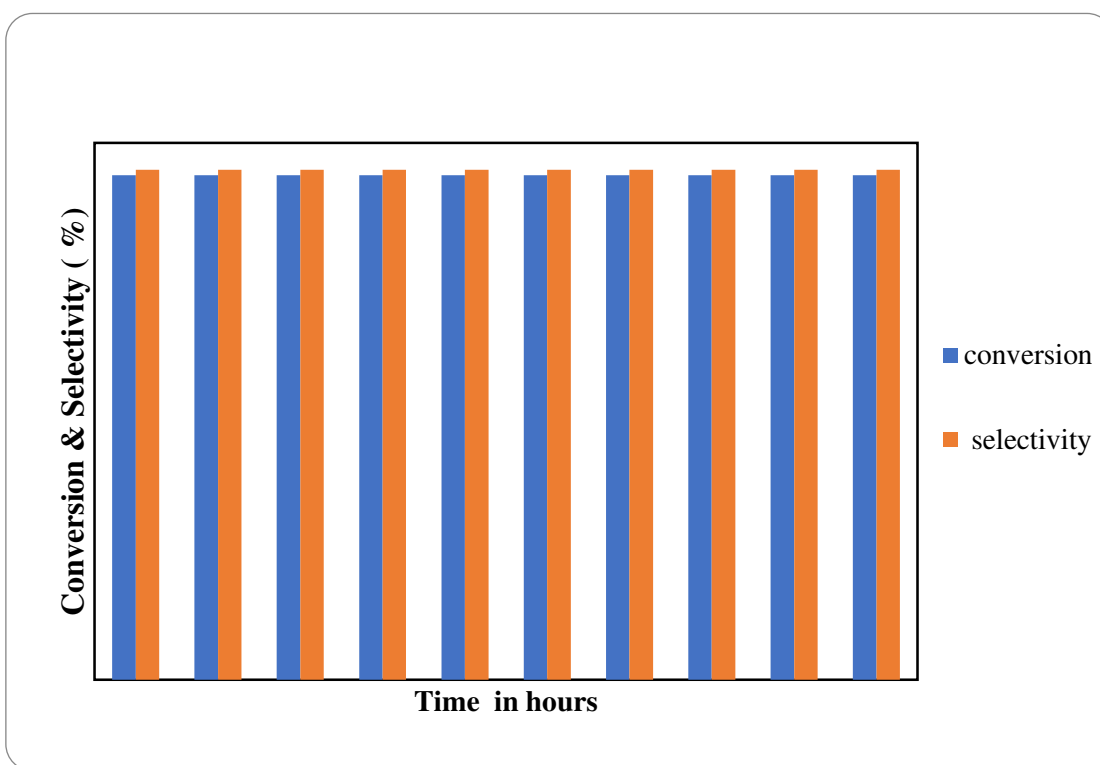
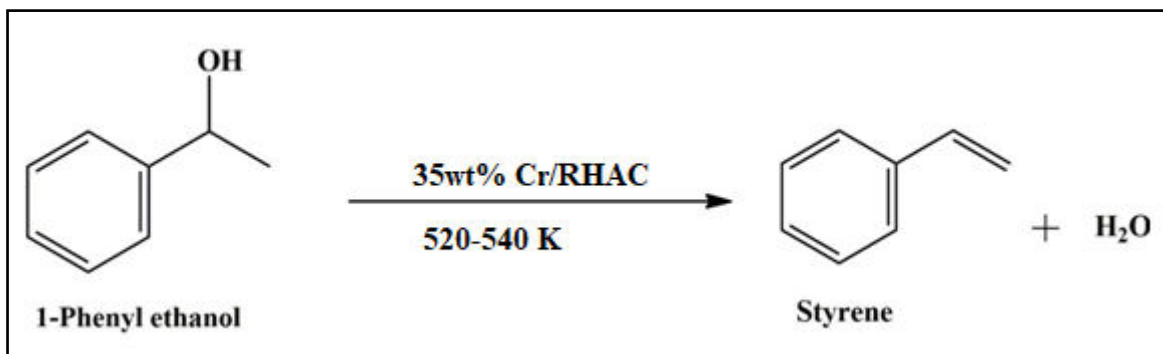


Fig: 5. Time on stream on 35wt. % Cr/RHA at 540 K up to 10 hours

#### 4.2 Dehydration on 1-phenylethanol to Styrene:

Catalyst activity of 35wt% Cr/RHAC has studied over dehydration of 1-phenylethanol in the temperature range of 520-540

K. Fig:6 show the transformation of 1-phenylethanol change over 35wt% Cr/RHAC in to Styrene.



**Fig.6.** Dehydration of 1-phenylethanol to styrene

Catalyst	Conversion %	Selectivity % of Styrene
Al <sub>2</sub> O <sub>3</sub>	90	95
TiO <sub>2</sub>	91.5	93.5
35wt % Cr/RHAC	95	95

**Table: 3.** Comparative study of dehydration reaction of 1-phenylethanol over previous reported catalysts.

The catalyst action of 35wt% Cr/RHAC has been contrasted and different rare earth metal oxides referred to in the writing [21] and the outcomes are condensed in Table: 3 Nonetheless, the time on stream action concentrate for 10 hours show a reduction of 1-phenylethanol transformation from 95% to 56% is seen over 35% Cr/RHAC might be

because of the arrangement of coke. These outcomes reason that the permeable structure with high surface area and higher acidic quality of Cr/RHAC favors higher conversion.

### 5. Conclusions:



➤ The above investigations summarized that the Chromium supported on mesoporous RHAC catalyzed the conversion of tetrahydrofuran and styrene through dehydration of 1, 4-butanediol and 1-phenylethanol individually.

➤ The reactant conversion and selectivity are firmly affected by requested permeable structure, high surface area and high acidic sites of 35wt% Cr/RHAC.

➤ Anyway the rate transformation of 1-phenylethanol to styrene is obviously superior to the change of 1, 4-butanediol. But the stability of the catalyst later reaction is more than the former reaction.

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