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Alumina-boron catalysts for oxidative dehydrogenation of ethylbenzene to styrene: Influence of alumina-boron composition and method of preparation on catalysts properties

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ABSTRACT

Different mole ratio Al-B catalysts (Al-10B to Al-35B) were synthesized by using sol-gel (SG) method. Ethyl benzene (EB) dehydrogenation in the presence of oxygen and water steam was carried out on these catalysts at 450–500 °C with EB contact time of 0.54 g_{cat}.cm⁻³. Acidity of Al-B catalysts was estimated by using NH₃-TPD-mass spectral analysis studies. SEM-mapping images revealed fine distribution of boron up to 15% of its loading in alumina (Al-15B), whereas, boron aggregation was observed in higher boron content (Al-25B and Al-35B) catalysts. Essentially, acid sites of very weak strength ($T_{\max} \leq 125$ °C) were observed for Al and Al-10B catalysts and resulted in low EB conversion and styrene yield. On the other hand, acid sites of weak strength ($T_{\max} \leq 180$ °C) were observed for Al-25B and Al-35B catalysts and resulted in high EB conversion. However, greater styrene yield (43.2%) with reasonable EB conversion (46%) was obtained on acid sites of weak moderate strength in Al-15B catalyst. Further, Al-15B catalyst was synthesized by using co-precipitation (COP) and impregnation (IMP) methods. Acid sites related to NO_x formation during the NH₃-TPD-mass analysis on IMP and COP catalyst essentially improved the EB conversion to 66% and 63% respectively at 500 °C. However, these acid sites were diminished in Al-B SG catalyst and resulted in 50% of EB conversion at 500 °C. At 50% of EB conversion level, styrene selectivity of 73%, 82.5% and 84% were observed on Al-B IMP, Al-B COP and Al-SG catalysts, respectively. Hence, different method of preparation of Al-B catalyst generated acid sites of different strength and density and thereby influenced the styrene formation.

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1. Introduction

Styrene is mainly used for the production of different polymeric materials such as polystyrene, styrene-acrylonitrile and acrylonitrile-butadiene-styrene (ABS) etc. [1–3]. Industrial styrene production is mainly associated with two technologies:

(1) dehydrogenation of EB in presence of steam over iron oxide based catalysts; (2) epoxidation of propene with ethylbenzene hydroperoxide on Mo complex-based catalysts. The first method covers about 90% of styrene consumption worldwide.

There are two points, which create problems in the practical realization of EB dehydrogenation. The dehydrogenation of EB

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is endothermic process. The separation of by-products is another problem of this process. Oxidative dehydrogenation (ODH) is one of the possible alternative routes. In this process water was formed as a by-product and EB dehydrogenation becomes the exothermic process. Therefore the process thermodynamically enables obtaining of the complete conversion of EB.

Various oxides [4,5] and phosphates [4–7] were used as catalysts for the ODH of EB. The carbonaceous layers formed on the catalysts surfaces were found to be catalytically active. The XPS and SIMS analysis of these carbonaceous layers has revealed the presence of quinone-like surface groups [8,9]. The proposed reaction mechanism involves the participation of oxygen atoms of quinone-like groups considered to be EB dehydrogenated to styrene and forming water as by-product [9,10]. The surface acidity of oxide catalyst plays a significant role in the formation of this active coke layer [11,12]. In general, Lewis acid sites of moderate strength were considered to form the active coke most effectively [6]. Many studies are available for ODH of EB using alumina as a catalyst [13–15]. Boron addition to alumina improved the acidity in Al-B catalysts [16,17].

Hence, in this paper, for the first time, we are reporting the influence of boron loading on the surface acidity of Al-B catalysts and its subsequent effect on styrene formation in ODH of EB reaction. Different mole ratio Al-B catalysts (Al-10B to Al-35B) were synthesized by sol-gel (SG) method. Based on the catalytic activity results, the optimized Al-15B composition was further prepared by two other methods namely co-precipitation (COP) and impregnation (IMP). The catalytic activity of these catalysts were compared to Al-15B SG results.

NH₃-TPD-mass analysis data was used to determine the acid sites distribution and acid sites behavior in all the studied Al-B catalysts. Further, the boron deposition in Al-B samples were studied through SEM-mapping. The ODH of EB to styrene using these catalysts was carried out at 450–500 °C with EB contact time of 0.54 g_{cat}.s.cm⁻³. Finally a correlation was drawn between the surface acidity and styrene yield on Al-B catalysts prepared in this study.

2. Experimental

2.1. Synthesis of Al-B catalysts

Sol-gel method (SG) different mole ratio Al-B catalysts were prepared by sol-gel (SG) method [17]. Aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O) solution was treated with ammonia gas for the synthesis of alumina. For example, 73.6 g of Al(NO₃)₃·9H₂O and 2.42 g of H₃BO₃ was used for 15 mol% of boron loading in Al (Al-15B). In separate beakers Al(NO₃)₃·9H₂O and H₃BO₃ was dissolved in 196 cm³ of ethanol and 25 cm³ of distilled water respectively. The resultant ethanol solution was stirred at 45 °C and the boric acid solution was stirred 100 °C for 1 h. At later stage, the boric acid solution was mixed with Al(NO₃)₃·9H₂O solution under continues stirring. A white turbid suspension was obtained after 1 h of stirring at 65 °C. The turbid suspension temperature was brought back to 25

°C with simultaneous passing of ammonia gas (99.99%) through it at a flow rate of 10 cm³ min⁻¹. The suspension turned into a thick white gel at pH = 6.2. To this gel, 100 ml of ethanol was added and the total gel solution was refluxed at 90 °C for 12 h. Finally, the obtained gel was dried in a preheated oven at 120 °C for 3 h under static air. Catalysts with different Al to B mole ratio were prepared accordingly.

Co-precipitation method (COP)

187.5 g of Al(NO₃)₃·9H₂O was dissolved in 250 ml of deionized water to get 2 M aluminum nitrate solution. To this solution approximately 6 g of boric acid was added. The mixture solution was stirred for 2 h at room temperature followed by the addition of 14.3 ml of acetic acid. At this stage, the measured pH was about 1. Drop wise ammonia solution (35.04 g mol⁻¹) was added to above solution until the pH reached to 6.3. The resultant solution was left at overnight reflux at about 95 °C until the gel formation. The obtained gel was dried overnight in a vacuum oven at 110 °C.

Impregnation method (IMP)

2.5 g of boric acid was added to 100 ml of deionized water and to this solution 25 g of neutral alumina (Acros) was added. The resultant mixture was aged for 1 h and the excess water was removed using hot plate. The solid particles were dried in a preheated oven at 110 °C for overnight.

All the dried samples were calcined at 600 °C for 20 h in static air. The numerical notification in the names of Al-B samples indicate the B mole percentage loading in Al.

2.2. Catalytic activity tests

Catalytic tests were performed at 450–500 °C with EB contact time of 0.54 g_{cat}.s.cm⁻³ (STP). The ratio between O₂ and EB was maintained at 0.9 and H₂O to EB ratio was kept at 4. The reaction mixture was analyzed by using HP 6890 GC connected to FID and TCD. O₂, CO and CO₂ were analyzed through TCD connected to a Molsieve and Porapak N columns. Methane, ethane, ethylene, benzene, toluene, EB and styrene were analyzed using FID connected to a Silcoport WAW column. EB conversion, styrene, other HC's (methane, ethane, ethylene, benzene and toluene) and CO_x selectivity was calculated according to following equations:

$$\% \text{ Conversion} = \frac{\text{moles consumed}}{\text{moles in the feed}} \times 100$$

$$\% \text{ Selectivity} = \frac{\text{moles of product}}{\text{moles of EB consumed}} \times 100$$

$$\% \text{ Styrene yield} = \text{EB conversion} \times \text{Styrene selectivity}$$

2.3. Characterization of catalysts

The BET surface area analysis of prepared samples was performed using Quantachrome Nova Station (USA). The samples were pretreated under vacuum for 2 h at 200 °C.

XRD analysis was done using EQUINOX 1000 Inel XRD machine at Co K_α = 1.7902 Å with acquisition of 2θ from 10° to 110°. XPS analysis of samples was done on SPECS GmbH analysis system containing Mg K_α 1253.6 eV X-ray source. The samples binding energy (BE) were attained by using C 1s 284.8 eV

correction.

NH₃-TPD-mass spectral analysis results of studied samples were obtained by using ChemBET Pulsar Quantachrome instrument. The mass spectral data was obtained by using ThermoStar™ GSD 320 quad core mass spectrometer. The m/z values which are followed were: $m/z = 17$ (NH₃), $m/z = 30$ (NO) and $m/z = 44$ (N₂O). In detail, calcined sample of 100 mg was placed in a quartz tube and pretreated at 200 °C in He flow (10 cm³ min⁻¹) for 2 h. Subsequently, the temperature of the sample was brought to 50 °C and saturated with 5 vol% NH₃-N₂ for 1 h. After this step the sample was flushed with He flow (10 cm³ min⁻¹) for 1 h. Desorption of probe gas was performed over the temperature range of 50–550 °C at a ramping rate of 10 °C min⁻¹. The desorption stream was analyzed simultaneously using a TCD and mass spectral detector by means of an automated split valve. Identical procedure was followed for the reference TPD-mass experiment except the step that involved sample saturation with 5 vol% NH₃-N₂ probe gas. Al-15B calcined sample prepared by using SG method was studied for reference TPD-mass experiment. SEM-mapping of Al-B samples was done using field emission scanning electron microscopy (FE-SEM, Quanta FEG450, FEI) using an Everhart Thornley detector (ETD, HV mode) and a solid-state back scattering electron detector (VCD). TG/DTG analysis was carried out on STA-449 F3, NETZSCH instrument by using 20 mg of spent sample loading. The measurements were done under air flow rate of 20 cm³ min⁻¹ at a temperature ramping rate of 5 °C min⁻¹.

3. Results and discussion

3.1. Catalytic activity and characterization of different mole ratio Al-B catalysts

Catalytic activity of different mole ratio Al-B SG catalysts are presented in Fig. 1. Alumina itself showed 32% of EB conversion with 18.5% of styrene yield at 475 °C. The conversion of oxygen and EB were increased with increase in the boron loading. The maximum oxygen (98%) and EB conversion (54%) were obtained on Al-35B catalyst. However, the obtained styrene yield was about 41.7% on this catalyst. The maximum styrene yield of 43.2% was observed on Al-15B catalyst with 46% of EB conversion. Whereas, styrene formation

Fig. 1. Catalytic activity of different mole ratio Al-B SG catalysts at 475 °C with EB contact time of 0.54 g_{cat}.S.cm⁻³.

was found low on Al-10B catalyst at 40% EB conversion. Further, CO_x formation was high on Al-25B (12%) and Al-35B (18%) catalysts.

NH₃-TPD-mass spectral analysis, XPS and SEM-mapping techniques were employed to characterize the different mole ratio Al-B SG catalysts to explain the activity differences for the studied reaction. Fig. 2 displays NH₃-TPD-mass spectral patterns of different mole ratio Al-B SG catalysts. The NH₃ desorption peaks for these catalysts were assigned to $T_{\max} \leq 120$ °C for acid sites of very weak strength; $T_{\max} \leq 180$ °C to acid sites of weak strength; and $T_{\max} \geq 250$ °C to acid sites of moderate strength. Two distinct desorption peaks were observed for Al, Al-10B and Al-15B catalysts. Acid sites of very weak strength were found high in Al to Al-10B samples. On the other hand, weak and moderate acid sites were developed in Al-15B sample. It is clear from the results that moderate acid site density was increased with increase of the boron loading up to 15%. Further increasing of the boron loading (25 mol% and 35 mol%) yielded a broad desorption peak in the temperature range of 50 to 300 °C with $T_{\max} = 180$ °C, which suggests acid sites of weak strength were dominant in Al-25B and Al-35B samples. It is well known that acid sites of weak moderate strength are major reason for the formation of active coke layer on the catalyst surface [6]. This active coke can influence the process of the dehydrogenation of EB to styrene. In case of Al and Al-10B samples, acid sites of very weak strength were dominating and resulted in low EB conversion and styrene yield. Furthermore, considerable amount of acid sites of weak and moderate strength in Al-15B catalyst showed 43.2% of styrene yield. The acid sites present in Al-25B and Al-35B catalysts had increased activity towards the CO_x formation. It is obvious from the Table 1 TG/DTA data that coke weight loss found high in Al, Al-25B and Al-35B spent samples. Higher CO_x formation on Al, Al-25B and Al-35B catalysts was attributed to the excess coke conversion to CO_x and or the decomposition of EB or styrene under ODH conditions.

Fig. 3 displays the SEM-mapping of Al-10B, Al-15B and Al-25B samples. Finely distributed boron particles (green color) were observed for samples up to 15 mol% of boron loading.

Fig. 2. NH₃-TPD-mass spectral analysis of different mole ratio Al-B samples.

Table 1

BET surface area, Acidity, TG/DTG and XPS analysis data for the samples with different Al-B ratios.

Catalyst	BET surface area (m ² ·g ⁻¹)	B and Al XPS surface atomic concentrations	NH ₃ -TPD acidity (μmol·g ⁻¹)			Styrene yield (%)	TG/DTG Wt. loss of spent Al-B (%)
			Very weak	Weak	Moderate		
Al	160	38% Al	190	—	20	18.5	11.0
Al-10B	214	2.4% B, 33% Al	342	—	40	32.0	6.5
Al-15B	290	4.4% B, 30% Al	—	360	120	43.2	7.5
Al-25B	232	5.3% B, 23% Al	—	491	—	40.7	8.4
Al-35B	202	7.8% B, 20% Al	—	510	—	41.7	9.0

Fig. 3. SEM-mapping images of different mole ratio Al-B samples Al-10B (a), Al-15B (b), and Al-25B (c).

Whereas, aggregation of boron particles were observed at higher boron content (see sample Al-25B). Table 1 presents BET surface areas, surface XPS concentrations, TG/DTA and acidity data for Al and Al-B samples. The BET surface area was decreased with increase of B loading in Al-B samples. The surface area changes were associated with the alumina pores blockage by B. The results are in agreement with SEM-mapping, wherein, aggregation of boron particles was observed at 25% of B loading (Al-25B). The surface XPS boron concentration was increased with an increase in the B loading and boron was existed in the form of B₂O₃ in all the studied Al-B samples.

Based on the styrene yield (Table 1), the optimized Al-15B catalyst was further synthesized by using IMP and COP methods. The catalytic activity and characterization results of these catalysts were further studied and compared to Al-15B SG catalyst at 450–500 °C. The detailed characterization analysis of these catalysts discussed further.

3.2. XRD

XRD patterns of B₂O₃, Al₂O₃ and Al-B catalysts synthesized by three different methods are presented in Fig. 4. All the Al-B catalysts showed X-ray patterns related to γ-Al₂O₃ phase at 2θ values of 43.5°, 54° and 79°. Pure B₂O₃ showed X-ray signals mainly at 2θ values of 32.5°, 36° and 46.2°. X-ray signals related to B₂O₃ were not detected in Al-B COP and Al-B SG catalysts. It could be due to the presence of small sized B₂O₃ particles below 4 nm in these catalysts. However, Al-B IMP catalyst displayed X-ray signals related to B₂O₃ at 2θ = 32.5°. XRD results clearly demonstrated that preparation method of Al-B catalyst influenced the size of boron crystals.

3.3. N₂ sorption isotherms and pore size distribution

N₂ sorption isotherms and pore size distribution results are

presented in Fig. 5. Essentially, isotherms of IUPAC type-IV was observed for all the three Al-B samples (Fig.5(a)). The results suggest the formation of mesoporous structure of samples with slit like pores. Pore size distribution results are presented in Fig. 5(b). It is obvious from the results that the pores were mainly distributed in the range of 4 to 9 nm, which suggests mesoporous nature of the studied Al-B samples. The average pore width for Al-B COP and Al-B SG samples were observed about 7 nm, whereas, the average pore width was about 5 nm for Al-B IMP sample. Further, highest total pore volume found in Al-B SG (0.509 cm³ g⁻¹) followed by Al-B COP (0.490 cm³ g⁻¹) and Al-B IMP (0.450 cm³ g⁻¹) sample. The decrease in the pore volume was associated with blockage of the part of alumina pores by B. The decreasing order of BET surface area of Al-B samples is as follows: Al-B SG (290 m² g⁻¹) > Al-B COP (238 m² g⁻¹) > Al-B IMP (210 m² g⁻¹) > Al (160 m² g⁻¹, 0.13 cm³ g⁻¹) > B₂O₃ (24 m² g⁻¹, 0.17 cm³ g⁻¹). The BET surface area and pore size distribution results suggests intact pore structure of Al

Fig. 4. XRD analysis of Al-B samples prepared by different method.

Fig. 5. N_2 sorption isotherms (a) and pore size distribution (b) of Al-B samples.

even after the addition of B to it.

3.4. NH_3 -TPD-mass spectral analysis

The NH_3 -TPD-mass analysis results of Al-B catalysts synthesized by three different methods are presented in Fig. 6. The mass value of $m/z = 17$ was assigned to ammonia and the corresponding mass analysis results are presented in Fig. 6(a). Two distinct desorption signals were observed for Al-B SG and Al-B COP catalysts at $T_{max} = 165$ and 250 °C respectively. However, Al-B IMP displayed a single desorption signal for ammonia at $T_{max} = 120$ °C. The results suggest the presence of very weak, weak and moderate acid sites in the studied Al-B samples.

Partially dehydrogenated ammonia species (NH_2^- , $m/z = 16$) followed by its decomposed products such as water and NO_x formation was reported by Hinz et al. [18] on alumina based catalysts. Nitric oxide (NO) mass spectral analysis of all the three Al-B catalysts are presented in Fig. 6(b). It is obvious from the results that ease formation of NO was observed on Al-B IMP over Al-B COP catalyst. On the other hand, NO formation was not detected on Al-B SG catalyst. Furthermore, N_2O mass spectral analysis results are reported in Fig. 6(c). Facile

N_2O formation was observed on Al-B IMP at about 200 and 350 °C. Whereas, a single N_2O signal was observed at 450 °C for Al-B COP catalyst. The mass signal for N_2O was totally diminished on Al-B SG catalyst. Hence, different method of preparation influenced the nature of acid sites and its effect on formation of by-products in the process of ODH of EB.

3.5. SEM-mapping

Fig. 7 displays the SEM images and mapping for all the three Al-B samples. Different particle morphology was observed for different method of preparation of Al-B catalysts. Flower petal like morphology was observed for Al-B SG catalyst. Whereas, plate and spherical shaped crystals were detected in Al-B COP and Al-B IMP catalysts respectively. Mapping data clearly demonstrates aggregation of B particles in Al-B IMP in agreement with XRD data. Whereas, finely distributed B particles were observed for Al-B SG and Al-B COP catalyst. However, isolated boron particles which are not present on the Al matrix were also observed in Al-B COP catalyst. These boron particles may present in the form of B_2O_3 in line with our XPS results. The SEM-mapping data revealed that the morphology and boron distribution was influenced by method of Al-B preparation.

Fig. 6. NH_3 -TPD-mass analysis results of Al-B catalysts.

Fig. 7. SEM-mapping images of Al-B IMP catalyst (a,b), Al-B COP catalyst (c,d), and Al-B SG catalyst (e,f).

3.6. Influence of the method of preparation on the catalytic activity

Influence of Al-B catalyst synthesis on EB conversion and styrene selectivity are presented in Fig. 8. The catalytic activity studies were performed in the temperature range of 450–500 °C with EB contact time of 0.54 g_{cat}.s.cm⁻³. EB conversion and CO_x formation was increased with increase in the reaction temperature on all the three studied catalysts. About 50% of EB conversion level, 84%, 82.5% and 73% of styrene selectivity was obtained on Al-B SG, Al-B COP and Al-B IMP catalysts respectively. The CO_x formation was high on Al-B IMP (40%) followed by Al-B COP catalyst (23%) and Al-B SG (12%) at 500 °C. Low amount of degraded products were observed on Al-B SG over other two studied catalysts under similar reaction conditions. NH₃-TPD-mass studies clearly demonstrated that acid

Fig. 8. Influence of Al-B catalyst preparation method on its activity in the temperature range of 450–500 °C with EB contact time of 0.54 g_{cat}.s.cm⁻³.

sites present in Al-B SG catalyst does not produced NO_x and hence showed greater styrene selectivity. On the other hand, acid sites which are forming NO_x were contributing to the conversion of excess coke and or EB/styrene decomposition to CO_x. Hence, catalyst synthesis method was playing a crucial role in tuning the acidity of the Al-B catalyst and thereby active coke formation and its resultant effect on styrene selectivity.

3.7. Styrene yield vs acidity

It is clear from Fig. 9 that styrene yield increased with increase in the total acidity of the Al-B catalyst. Among the stud-

Fig. 9. Al-B catalyst acidity versus styrene yield at 475 °C.

ied catalysts, greater styrene yield (43.5%) was obtained on Al-B COP catalyst followed by Al-B SG (43.2%) and Al-B IMP (40.8%). The improved styrene yield for Al-B COP and Al-B IMP catalysts were associated with their improved EB conversion. The greater EB conversion on these catalysts was associated with the formation of the type of acid sites active for NO_x generation. Further, ease formation of NO_x was observed on Al-B IMP catalyst over Al-B COP catalyst which showed the greater conversion of EB (66%) mostly to CO_x. Hence, acid site density and acid site nature is important for styrene yield.

4. Conclusions

At lower boron loading very weak acid sites were generated and resulted in low EB conversion and styrene yield. At higher boron loading (Al-25B or Al-35B) weak acid sites were responsible for improved EB conversion. The optimized Al-B ratio found to be at 15% of boron loading which showed 43.2% of styrene yield with 46% of EB conversion at 475 °C. Among the

method of preparations Al-B COP catalyst showed greater styrene yield of 43.5% with 60% of EB conversion at 475 °C. Acid sites responsible for NO_x formation during NH₃-TPD-mass analysis were improved the EB conversion. About 50% of EB conversion level, 84%, 82.5% and 73% of styrene selectivity was obtained on Al-B SG, Al-B COP and Al-B IMP catalysts, respectively. Hence, method of preparation influenced the product distribution in EB to styrene ODH reaction in the presence of oxygen and water steam.

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Graphical Abstract

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Boron addition to Al improved the acidity of the Al-B catalysts. Styrene formation depends on the nature of acid sites which were influenced by the Al-B catalyst method of preparation.

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用于乙苯氧化脱氢制苯乙烯铝-硼催化剂： 铝硼组成及制备方法对催化剂性能的影响

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摘要: 采用溶胶-凝胶(SG)法合成了不同摩尔比的Al-B催化剂(Al-10B与Al-35B)。在450–500 °C, 乙苯(EB)接触时间为0.54 g-cat.s.cm⁻³的条件下, 在氧气和水蒸气存在下对这些催化剂进行催化乙苯脱氢反应。利用NH₃-TPD质谱分析了Al-B催化剂的酸性。扫描电镜图像显示, 硼在氧化铝中负载量达15%(Al-15b)时仍分布很好, 而在较高的硼含量(Al-25B和Al-35B)催化剂中观察到硼聚集。从本质上讲, 在Al和Al-10B催化剂上观察到强度非常弱($T_{\max} \leq 125$ °C)的酸位, 使得EB转化率和苯乙烯产率很低。另一方面, 在Al-25B和Al-35B催化剂酸位较弱($T_{\max} \leq 180$ °C), 因而EB转化率较高。然而, 在弱-中等强度酸位的Al-15B催化剂上可以得到较高的苯乙烯产率(43.2%)和合理的EB转化率(46%)。另外, 采用共沉淀法(COP)和浸渍法(IMP)合成了Al-15B催化剂。IMP和COP催化剂的NH₃-TPD-质谱分析结果发现, 与NO_x形成有关的酸位点在500 °C时将EB转化率分别提高到66%和63%。然而, Al-B SG催化剂中的这些酸位降低, 使得500 °C时EB转化率为50%。当EB转化率为50%时, 在Al-B IMP, Al-B COP和Al-SG催化剂上苯乙烯选择性分别为73%, 82.5%和84%。因此, 不同方法制备的Al-B催化剂, 会产生不同强度和密度的酸位, 从而影响苯乙烯的形成。

关键词: 铝-硼; 氧化脱氢; 乙苯; 苯乙烯; 共沉淀

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