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Pore-engineered silica–alumina: texture, acidity, and activity for conversion of longifolene to isolongifolene

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Abstract Pore-engineered silica–alumina was synthesized for the conversion of longifolene to isolongifolene, and the effects of texture and surface properties on the activity were examined. The acidity and texture of the modified silica–alumina play a vital role in governing the catalytic isomerization of longifolene to isolongifolene. A conversion of 97% of longifolene with 95% selectivity has been achieved.

Keywords Silica–alumina · Longifolene · Isolongifolene · Acidity · Surface area distribution · Pore size distribution

Introduction

Aluminosilicate catalysts find application in various types of reactions like cracking, acylation, alkylation, dealkylation, cyclodehydrogenation, isomerization, and other acidcatalyzed reactions [1–9]. Proper choice of the surface characteristics of a catalyst can increase activity, selectivity, and catalyst life. In aluminosilicate catalysts, acid sites generated by substitution are responsible for the catalytic

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S. K. Ray CIMFR, Dhanbad, Jharkhand, India activity. Tetrahedral Al atoms in the silica network are assumed to be highly active components in aluminosilicates. Aluminum has only three valence electrons, whereas silicon has four. Substitution of silicon by aluminum in the tetrahedron therefore creates a vacancy which is filled by accommodating an electron and a negative charge is thus obtained. Compensation of the resulting negative charge by a proton gives rise to a Brønsted acid site [10]. Lewis acid sites usually predominate on dehydrated silica–alumina although adsorbed water leads to the conversion of Lewis to Brønsted acid sites [11, 12].

In the present work, pore-regulated silica–alumina was synthesized by a stepwise precipitation technique using pore-regulating agents (PRAs) such as tetraalkylammonium salts (methyl, ethyl, propyl, and butyl) and the texture and surface properties were determined. An attempt was made to correlate these properties with activity in the transformation of longifolene to isolongifolene through acid-catalyzed isomerization reaction (Scheme 1).

Longifolene (C₁₅H₂₄, decahydro-4,8,8-trimethyl-9methylene-1,4-methanoazulene), a tricyclic sesquiterpene hydrocarbon, is a commercially important chemical whose oxygenated derivatives (e.g., alcohols, ketones, oxides, aldehydes) have been extensively used in the perfumery and pharmaceutical industries because of their woody and floral notes [13, 14]. Several investigations were reported on the conversion of longifolene to isolongifolene using acids like sulfuric acid/acetic acid [15], BF₃·OEt₂ [16, 17], bromoacetic acid [18], camphenecarboxylic acid [19], and others [20, 21]. The disadvantages inherent in the use of acids are multiple steps, long reaction times, and above all the existing processes are not eco-friendly [15]. Moreover other rearranged products such as tetralin and octal are also formed as side products [22]. The catalyst prepared in the current paper has better activity, selectivity, and

Longifolene

Scheme 1

recyclability as compared to conventional catalysts [23, 24]. In our earlier work [25] an attempt was made to correlate the activity of the catalysts with total acidity, number, and strength of the acids for the conversion of longifolene to isolongifolene with 70–80% conversion. In the present work we studied the role of acidity and morphology of the modified silica–alumina for catalytic isomerization of longifolene to isolongifolene, and 97% conversion of longifolene with 95% selectivity has been achieved.

Results and discussion

Compositions of the catalysts and their specific surface area, pore volume, and pore size distribution are summarized in Table 1. The morphological aspects of the samples are shown in Figs. 1, 2, 3, and 4. The results show that surface area, pore size, and morphological properties of silica–alumina are greatly influenced by various factors like method of preparation, pH, silica to alumina ratio, synergism, ageing, etc. It is believed that the pore-regulating effect of PRAs is based on the volume occupied at the molecular level in the gel before removal of components by combustion or evaporation [26]. The tetraalkylammonium cations decompose after combustion or evaporation releasing alkaline material [27].

Figure 1 shows that the silica–alumina aggregate prepared without PRA has a pore size distribution of 700–750 nm and the aggregates are not spherical in shape. Figure 2 shows that when the sample is prepared with tetramethylammonium (TMA) compound, the size of



Fig. 1 SEM of SiO₂-Al₂O₃ (without PRA)

aggregate is about 350–400 nm and particles are more or less spherical in shape, whereas in the sample prepared with tetraethylammonium (TEA) compound the size of aggregate as shown in Fig. 3 is 400–550 nm.

Table 1 reveals that the maximum surface area for samples prepared without PRA is 278.5 m² g⁻¹. On treatment with PRA the surface area is sharply reduced because the carbon number in the alkyl group influences the surface area as well as texture properties of the silica–alumina catalyst. It is interesting to observe that the surface area of samples prepared from TMA to tetrapropylammonium (TPA) gradually increases with the increase of carbon number in the alkyl group but suddenly declines to 102.2 m² g⁻¹ for the sample prepared with tetrabutylammonium (TBA) compounds, which is not in accordance with the finding made by Manton and Davidtz [28]. This may be due to differences in preparation methods, the source materials, pH, and product concentration, which affect the surface area to some extent [29]. Table 1 also

 Table 1
 Surface area, pore volume, and pore size distribution of different catalysts

Catalyst	Surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹	Pore size distribution/nm						
			0.4–6	6–10	10-20	20-30	30–40	40–50	>50
SiO ₂ -Al ₂ O ₃ without PRA, stepwise	278.5	1.0301	73.2	12.8	6.9	2.6	0.9	1.0	2.6
SiO ₂ -Al ₂ O ₃ with TMA	126.5	0.9012	31.7	8.7	12.4	10.9	6.9	7.0	22.4
SiO ₂ -Al ₂ O ₃ with TEA	129.5	1.4878	9.5	3.3	7.0	7.6	3.6	6.2	62.8
SiO ₂ -Al ₂ O ₃ with TPA	179.1	1.2905	9.1	7.6	14.8	11.4	8.1	15.9	33.1
SiO ₂ -Al ₂ O ₃ with TBA	102.2	1.4302	12.5	3.8	2.8	2.8	6.1	13.6	58.4

TMA tetramethylammonium, TEA tetraethylammonium, TPA tetrapropylammonium, TBA tetrabutylammonium





Fig. 2 SEM of SiO₂-Al₂O₃ with TMA as PRA



Fig. 3 SEM of SiO₂-Al₂O₃ with TEA as PRA

shows that the pore volume of SiO_2 -Al₂O₃ prepared without any PRA treatment is 1.0301 cm² g⁻¹ and 73.2% of pores are observed to be of diameter between 0.4 and 6 nm.

Table 2 shows that total acidity and acid distribution undergoe appreciable change and exhibit different strengths of acidity. It may be assumed that the PRA affects the acidic properties, pore structure, and surface area of silica–alumina gels because of the volume vis-à-vis the charge density of the respective PRA. NH₃ temperature



Fig. 4 SEM of SiO₂-Al₂O₃ with TBA as PRA

programmed desorption (TPD) results show that without PRA, the total acidity of the catalyst $m(H^+)$ is 1.10 mmol g^{-1} . The activity in terms of selectivity of isolongifolene is 50%, whereas conversion of longifolene is 48%. Modified with TMA compound produces a total pore volume of 0.9012 cm³ g⁻¹ and 31.7% of pores are of diameter 0.4-6 nm. NH₃ TPD shows that total acidity after modification increases to 1.18 mmol g^{-1} , comprising weak acidity 1.15 mmol g^{-1} , moderate acidity 0.01 mmol g^{-1} , and strong acidity 0.02 mmol g^{-1} . Selectivity of isolongifolene sharply increased to 82% and total conversion of longifolene is 84%. When Si-Al is modified with TEA, TPA, and TBA compounds, the acid strength and number of acidic sites subsequently change. Total acidity with TEA compound is 1.14 mmol g^{-1} comprising 98.38, 0.81, and 0.81% of weak, moderate, and strong acid sites, respectively, and total pore volume observed is $1.4878 \text{ cm}^3 \text{ g}^{-1}$ where 62.8% of pores are of diameter greater than 50 nm and selectivity of isolongifolene enhances very appreciably to 95% with 97% conversion. The enhanced selectivity and conversion are probably due to the acidity and distribution of pores. When modified with TPA compound, total acidity increases to 1.35 meq H^+ g^{-1} , where weak acid concentration is 92.71%, moderate 3.68%, and strong 3.61% (Table 2). Total pore volume slightly decreases to 1.2905 cm³ g⁻¹ and 33.1% of pores are of diameter above 50 nm. Selectivity of isolongifolene slightly decreases to 81.5% and conversion of longifolene is 90%.

When modified with TBA compound as the PRA, noticeable changes are observed in the number of acidic sites and strength of acidity. Total acidity is 1.58 mmol g^{-1} and concentrations of weak and moderate acid sites are 95.56 and 4.44%, respectively. Selectivity to isolongifolene sharply declines to 58% and conversion of longifolene decreases to

Catalyst	Weak acidity/ mmol g ⁻¹	Moderate acidity/	Strong acidity/	Total acidity/	Activity		
		mmol g	mmol g	mmol g	Conversion/%	Selectivity/%	
SiO ₂ -Al ₂ O ₃ without PRA, stepwise	1.10 (100.00)	0.00	0.00	1.10	48	50	
SiO ₂ -Al ₂ O ₃ with TMA	1.15 (97.46%)	0.01 (0.90%)	0.02 (1.64%)	1.18	84	82	
SiO ₂ -Al ₂ O ₃ with TEA	1.12 (98.38%)	0.01 (0.81%)	0.01 (0.81%)	1.14	97	95	
SiO ₂ -Al ₂ O ₃ with TPA	1.26 (93.33%)	0.05 (3.71%)	0.049 (2.9%)	1.35	81.5	90	
SiO ₂ -Al ₂ O ₃ with TBA	1.51 (95.56%)	0.07 (4.44%)	0.00 (0%)	1.58	75	58	

Table 2 Effect of total acidity and acid concentration on conversion and selectivity (GC yields)

75%. From Table 1 it is observed that the diameter of pores and pore volume are very near to those of Si–Al modified with TEA compound. The change in activity is probably due to a change in number and strength of acidity as well as the texture properties of the catalyst as observed from both Tables 1 and 2. So it may be assumed that volume vis-à-vis the charge density of the respective PRA highly influences the activity of the catalyst.

Catalyst recyclability

The catalyst recyclability was tested by conducting the reactions using the Si–Al modified with TEA compound as the PRA under optimized reaction conditions and the samples for analysis were collected after each hour. It is interesting to note that there is no significant loss in catalytic activity up to 2 h. The spent catalyst was regenerated after each 2 h and reused. The catalytic activity was almost similar to that of the fresh catalyst. The results obtained are shown in Fig. 5.

Thus it is evident from the above studies that the size of the PRA cations affects the texture and catalytic properties of silica–alumina, particularly total acidity, and generates different acid sites. Silica–alumina prepared with TEA compounds has the maximum selectivity for the production of isolongifolene through isomerization of longifolene. This may be ascribed to the characteristic morphology as well as the required total acidity and acid distribution. Thus, for an active, selective, and stable catalyst based on modified silica–alumina, compromising between distributions, concentration, and total acid strength with characteristic morphology of the catalyst is essential.

Experimental

Materials

Sodium silicate (99.95%), aluminum sulfate hexadecahydrate (98%), sodium hydroxide (98%), tetramethylammonium hydroxide (25% aq. solution), tetraethylammonium bromide



Fig. 5 Recyclability of the catalyst

(99%), and tetrabutylammonium bromide (98%) were purchased from Loba Chemie L.R. Tetrapropylammonium bromide (99%) was obtained from Merck-Schuchardt, sulfuric acid (7%) from BDH L.R, and hydrochloric acid (min. 35%) from Glaxo A.R.

Preparation of silica–alumina and modified silica–alumina

Silica gel was prepared by adding H_2SO_4 to a hot solution of Na₂SiO₃·5H₂O with vigorous stirring until the pH reached 7. Alumina gel was prepared by adding NH₄OH (1:1) to Al₂(SO₄)₃·16H₂O solution with vigorous stirring until pH reached 7.5–8.5. Both gels were aged for 1 h and then filtered and washed to free them from sulfate ions. Pore-regulated silica–alumina was synthesized by dissolving silica gel and alumina gel as prepared and dissolved separately in measured amounts of aqueous solution of the PRA and concentrated solution of sodium hydroxide. The two solutions were mixed thoroughly and a gel of silica– alumina was prepared at pH 9. The gel was then aged for 24 h, washed, and base exchanged with 2% ammonium nitrate solution. The mass was dried in air in an oven at 110 $^{\circ}$ C and finally calcined at 450 $^{\circ}$ C for 3–4 h.

Experimental set-up

The experiments for vapor-phase reactions were performed in a fixed-bed continuous flow reactor. The arrangement for testing the catalytic activity is described elsewhere [30] except that, instead of top feeding, bottom feeding was used. The vapors of longifolene and nitrogen were introduced from separate inlets. All the experiments were carried out between 160 and 200 °C.

GC analysis

GC analysis with respect to isolongifolene conversion was carried out on a Nucon 5765 gas chromatograph equipped with a flame ionization detector (FID) and AIMIL chromatography data processor. The separation was achieved using a FFAP, SE-30 fused-silica capillary column $(20 \text{ m} \times 0.25 \text{ mm i.d.}, 0.25 \text{ µm film thickness})$; column temperature 90 °C (2 min) to 220 °C at 4 °C/min; injection temperature 240 °C; detector temperature 260 °C; using split mode, and helium as carrier gas with column flow rate of 1.05 cm³/min (100 kPa). Retention indices (RI) of the sample components and authentic compounds were determined on the basis of homologous *n*-alkane hydrocarbons (n-nonane to n-nonadecane) under the same conditions. The quantitative analysis was determined by peak area normalization, and the response factor for each component was considered to be equal to 1.

Catalyst characterization

TPD experiments were performed after NH₃ adsorption on sample by a Chemisorbs 27820 (Micrometrics, USA) instrument. A 0.02- to 0.03-g sample was loaded in a quartz microreactor. Sample was dried in a flow of ultra pure argon (20 cm³/min) for 2 h at 200 °C then was saturated with NH₃ by flowing 10% NH₃ in helium at room temperature and normal pressure. The saturation of the catalyst with NH₃ was confirmed by the stability of the thermal conductivity detector (TCD) baseline. The sample temperature was then ramped to 550 °C at a linear heating rate at 5 °C/min in flowing helium (20 cm³/min). Desorption of NH₃ was measured with a TCD. Data were analyzed with the help of the Chemi software. The surface area of the catalyst samples was measured by adsorption of nitrogen with help of a Brunauer– Emmett–Teller (BET) apparatus at liquid N₂ temperature. Pore size distributions of catalysts were determined by using an AMNICO slow mercury porosimeter. The prepared samples were screened in a JEOL-100 CXII electron microscope with ASID at 40 kV and images are presented in Figs. 1, 2, 3, and 4.

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