固载化 AlCl_3 催化剂上 α -蒎烯异构化反应

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摘要: 分别以 SiO_2 和 $\gamma\text{-Al}_2\text{O}_3$ 为载体采用两步气相法制备了固载化 AlCl_3 催化剂, 并首次将其用于 α -蒎烯液相异构化反应. 结果表明, 该催化剂对 α -蒎烯异构化反应具有非常高的催化活性, 其中 $\text{AlCl}_3/\text{SiO}_2$ 催化剂在 40°C 反应时 α -蒎烯转化率和主产物 (蒎烯、柠檬烯和异松油烯) 选择性分别为 98.4% 和 93.7%; $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$ 催化剂活性更高, 在 30°C 反应时, 即可获得 95.5% 的 α -蒎烯转化率和 94.4% 的主产物选择性. 固载化 AlCl_3 催化剂的高活性与其强酸性有关.

关键词: 固载化; 三氯化铝; α -蒎烯; 异构化; 硅胶; 氧化铝

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Isomerization of α -Pinene over Immobilized AlCl_3 Catalysts

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Abstract: Immobilized AlCl_3 catalysts supported on $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 were prepared by a two-step vapor method and their catalytic activities were evaluated by the liquid phase isomerization of α -pinene for the first time. The results showed that the immobilized AlCl_3 catalyst gave excellent catalytic performance for the isomerization of α -pinene. The $\text{AlCl}_3/\text{SiO}_2$ catalyst gave 98.4% conversion of α -pinene and 93.7% selectivity for the main products such as camphene, limonene, and terpinolene at a reaction temperature of 40°C . The $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst gave much higher activity, 95.5% conversion of α -pinene and 94.4% selectivity for the main products even at temperatures as low as 30°C . The excellent catalytic performance of the immobilized AlCl_3 catalysts is due to their strong acidity.

Key words: immobilization; aluminum chloride; α -pinene; isomerization; silica; alumina

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松节油是世界上产量最大的一种天然芳香油, 在我国资源丰富, 年产量居世界第二, 但多以原料形式出口或直接使用, 如作为溶剂、稀释剂、油漆及医用皮肤刺激剂等, 这样就使其潜在价值未能得到开发和利用^[1]. 松节油主要成分为 α -蒎烯, 它具有特殊的双环结构和环内双键, 因而化学性质非常活泼, 尤其对酸特别敏感, 通过异构化、酯化和聚合等反应得到多种精细化学品^[2]. 在酸催化作用下 α -蒎烯异构化产物(图式 1)是制备香料、药物和精细化学品的重要中间体: 如其扩环产品蒎烯是合成樟脑、檀香和毒

杀芬等的主要原料, 其开环产物柠檬烯除本身具有抗癌作用外, 还可以进一步合成香芹酮、高熏衣草醇和薄荷醇等几十种香料. 因此, 对松节油资源进行高附加值转化具有明显的经济效益.

用于 α -蒎烯异构化反应的固体酸催化剂种类很多, 如金属氧化物^[3]、杂多酸^[4]、离子交换树脂^[5]、粘土^[6]、固体超强酸^[7]和沸石分子筛^[8~10]等. 但由于 α -蒎烯异构化反应产物复杂, 原料的转化率和高附加值产物的选择性往往不能同时兼顾. 因此, 在相对温和的反应条件下, 寻找一种高性能、低成本且环境

图式 1 α -蒎烯异构化反应路线Scheme 1. Reaction pathway for α -pinene isomerization^[2].

友好的催化剂以提高 α -蒎烯转化率和高附加值产物的选择性成为研究热点. 固载化 AlCl_3 催化剂是一种环境友好、活性高的固体酸催化剂, 已在烷基化和异构化反应中表现出独特的催化性能^[11~14]. 本文首次将固载化 AlCl_3 催化剂用于 α -蒎烯异构化反应, 在温和的反应条件下获得了很高的催化活性和主产物(莰烯、柠檬烯和异松油烯)选择性.

采用两步气相法制备固载化 AlCl_3 催化剂. 首先将载体 $\gamma\text{-Al}_2\text{O}_3$ (中国石化长岭炼油化工有限责任公司) 在 N_2 气氛中于 400°C 处理 2 h. 将 CCl_4 与纯度较高的 $\gamma\text{-Al}_2\text{O}_3$ 在 500°C 反应生成 AlCl_3 蒸气, 由 N_2 带入反应器, 与上述载体在 300°C 进行表面固载化反应 3 h, 然后在 400°C 用 N_2 将催化剂表面未反应和物理吸附的 AlCl_3 吹扫干净, 冷却至室温备用, 记为 $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$. 制备 $\text{AlCl}_3/\text{SiO}_2$ 催化剂时, SiO_2 (青岛海洋化工厂) 的预处理温度、固载温度以及吹扫温度均为 300°C , 其他同上. 催化剂中氯含量采用电位滴定法测定. 异构化反应在间歇式搅拌反应器中进行, 将 0.10 g 催化剂和 2 ml α -蒎烯 (Aldrich, 98%) 加入到

反应器中, 在不同温度下反应一定时间后, 将催化剂与反应液过滤分离. 反应产物采用 GC7890F 型气相色谱仪 (HP-5 毛细管柱, FID 检测器) 和 HP 6890N-5975B 型气质联用仪分析. 采用面积归一化方法定量, 并计算 α -蒎烯转化率和产物选择性.

化学分析表明, 载体 SiO_2 和 $\gamma\text{-Al}_2\text{O}_3$ 上 $[-\text{O}-\text{AlCl}_2]$ 的固载量分别为 10.6% 和 8.5%. 相关研究^[15,16]表明, 活性组分的固载是通过 AlCl_3 与载体表面羟基发生反应而实现的, 催化剂表面 90% 的活性位具有 $[-\text{O}-\text{AlCl}_2]$ 结构. 因此, 本文中两种载体表面上 $[-\text{O}-\text{AlCl}_2]$ 含量的差异可能是其表面羟基浓度不同所致.

表 1 为反应温度对 $\text{AlCl}_3/\text{SiO}_2$ 催化剂上 α -蒎烯异构化反应性能的影响. 可以看出, 在 $30\sim60^\circ\text{C}$ 范围内, 随着温度的升高, α -蒎烯转化率明显提高, 在 60°C 反应 30 min, α -蒎烯几乎完全转化, 说明该催化剂对 α -蒎烯异构化反应具有很高的催化活性. 但在 60°C 反应, 高保留值产物增加, 莰烯尤其柠檬烯的选择性明显下降, 说明在相对较高的反应温度下, 柠檬烯

表 1 固载化 $\text{AlCl}_3/\text{SiO}_2$ 催化剂对 α -蒎烯异构化反应的催化性能Table 1 Catalytic performance of the immobilized $\text{AlCl}_3/\text{SiO}_2$ catalyst during α -pinene isomerization

Entry	Reaction time (min)	Reaction temperature ($^\circ\text{C}$)	Conversion (%)	Selectivity (%)			
				Camphene	Limonene	Terpinolene	Others
1	30	30	40.0	31.7	56.8	8.1	3.4
2	30	40	75.0	31.3	56.0	9.1	3.6
3	30	50	88.0	30.2	55.3	9.8	4.7
4	30	60	99.8	28.5	46.7	13.4	11.4

发生深度反应转变成 α -和 γ -松油烯(见图式1). 当在较低的反应温度下延长反应时间(见图1), α -蒎烯转化率明显提高, 而茨烯和柠檬烯选择性几乎不变. 如

图1 40 °C 时 $\text{AlCl}_3/\text{SiO}_2$ 催化剂上反应时间对 α -蒎烯异构化反应性能的影响

Fig. 1. Effect of reaction time on α -pinene isomerization over the $\text{AlCl}_3/\text{SiO}_2$ catalyst at 40 °C. (1) Conversion of α -pinene; (2) Selectivity for camphene; (3) Selectivity for limonene; (4) Selectivity for terpinolene.

在 40 °C 反应 120 min, 可获得 98.4% 的 α -蒎烯转化率和 93.7% 的主产物选择性.

表 2 为 $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$ 催化剂上 α -蒎烯异构化反应结果. 可以看出, $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$ 催化活性比 $\text{AlCl}_3/\text{SiO}_2$ 的更高, 在 30 °C 反应 30 min, α -蒎烯转化率和主产物选择性分别即可达到 80.6% 和 96.5%. 当反应温度提高到 45 °C 时, 即可完全反应, 且此时主产物选择性仅略有下降. 同样, 在较低的反应温度下延长反应时间, 可以获得 95.5% 的 α -蒎烯转化率和 94.4% 的主产物选择性(表 2, 实验 4).

催化剂表面酸性研究表明^[17,18], 固载化 AlCl_3 催化剂表面分布着大量较强的 Lewis 酸和 Brønsted 酸中心. Özkan 等^[19]研究表明, α -蒎烯在 Lewis 酸位上更易于发生扩环反应, 在 Brønsted 酸位上更易于发生开环反应, Lewis/Brønsted 比值的变化可以改变产物分布. 本文制备的固载化 AlCl_3 催化剂对 α -蒎烯异构化反应具有很高的催化活性, 正是其具有强酸性的体现.

表 2 固载化 $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$ 催化剂上 α -蒎烯异构化反应的催化性能

Table 2 Catalytic performance of the immobilized $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst during α -pinene isomerization

Entry	Reaction time (min)	Reaction temperature (°C)	Conversion (%)	Selectivity (%)			
				Camphene	Limonene	Terpinolene	Others
1	30	30	80.6	41.2	53.9	1.4	3.5
2	30	40	96.4	40.6	52.7	1.7	5.0
3	30	45	100.0	40.6	52.5	1.8	5.1
4	60	30	95.5	41.6	51.3	1.5	5.6

综上所述, 固载化 AlCl_3 催化剂是一种可以高效催化 α -蒎烯异构化反应的新型环境友好固体酸催化剂. 后续工作将在载体性质的调变方面开展, 通过 Lewis 酸和 Brønsted 酸的相对酸量和酸强度的调变, 以期提高某单一产物的选择性, 为松节油的高附加值利用提供实验依据.

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英 译 文

English Text

α -Pinene is the main component of turpentine, which is the most abundantly produced natural essential oil in the world. Although turpentine has been used directly and extensively as a solvent, a diluent, and a skin irritant etc., more attention should be paid to the exploitation and utilization of its potential value [1]. α -pinene, as one of the most important bicyclic monoterpenes, is a very reactive substrate because of its unique structure. A large number of fine chemicals and raw materials have been obtained by these acid catalyzed reactions such as the isomerization, esterification, and polymerization of α -pinene [2]. The products obtained by the acid catalyzed isomerization of α -pinene are important intermediates for perfumes, pharmaceuticals, flavors, and fine chemicals. For example, camphene is obtained by ring expansion and is the main raw material for the synthesis of compounds such as camphor, santal, and toxaphene. Limonene is obtained by ring opening and it possesses an anti-tumor effect but it can also be used to synthesize many perfumes such as carvone, lavender alcohol, and menthol (Scheme 1). Therefore, it is of great economic interest to transform turpentine into high value products.

Various types of catalysts such as metal oxides [3], heteropolyacids [4], ion exchanged resins [5], clays [6], solid superacids [7], and micro- or mesoporous molecular sieves [8–10] have been investigated for the isomerization of α -pinene. Considering that industrial α -pinene isomerization is an energy consuming process and that the conversion of α -pinene and the selectivity toward the target products with high values cannot usually be achieved simultaneously because of the complexity of this reaction, further study is necessary to find effective catalysts that will function under mild reaction conditions. Therefore, developing an environmentally friendly catalyst with high performance, low cost, and high selectivity toward the main products is the main objective of much research. Immobilized AlCl_3 catalysts, which give unique catalytic performance for aromatic alkylation and olefin polymerization [11–14] are a type of environmentally friendly and high activity solid acid catalyst. This paper, for the first time, reports on the isomeriza-

tion of α -pinene upon catalysis by immobilized AlCl_3 catalysts, which showed high catalytic performance and selectivity toward the main products such as camphene, limonene, and terpinolene under mild conditions.

The immobilized AlCl_3 catalysts were prepared by a two-step method. Silica gel and $\gamma\text{-Al}_2\text{O}_3$, which are produced by the Qingdao Haiyang Chemical Plant Co. and the Changling Petrochemical Refining Co., China, respectively, were used as supports. First, the $\gamma\text{-Al}_2\text{O}_3$ support was dehydrated at 400 °C in a lower reactor under a N_2 stream for 2 h before use. The AlCl_3 that was produced in situ by the reaction between CCl_4 and pure $\gamma\text{-Al}_2\text{O}_3$ in an upper reactor at 500 °C was carried into the lower reactor by a N_2 stream and it was immobilized on the pretreated support at 300 °C for 3 h. After that, excess and physically adsorbed AlCl_3 was removed by flowing N_2 at 400 °C. Finally, the immobilized catalysts were cooled to room temperature under N_2 protection and the resultant catalyst was denoted $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$. A catalyst supported on SiO_2 was also prepared as per the above description except that the pretreatment and the purging process were carried out at 300 °C. The resultant catalyst was denoted $\text{AlCl}_3/\text{SiO}_2$. The chloride content of the catalyst was determined by potentiometric titration. The isomerization reaction was carried out at atmospheric pressure in a glass reactor with a reflux condenser under continuous magnetic stirring. For a typical run, 0.10 g of the catalyst and 2 ml of α -pinene (Aldrich, 98%) were charged into the reactor. The reaction time and temperature were investigated systematically. The samples were analyzed using a gas chromatograph equipped with a flame ionization detector (FID) and a HP 6890N-5975B (GC-MS). The conversion of α -pinene and selectivity toward the products were obtained by the area normalization method.

The chemical analysis results indicate that the mass fractions of $[-\text{O}-\text{AlCl}_2]$ on SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ were 10.6% and 8.5%, respectively. Previous studies have shown that the immobilization of AlCl_3 onto the surface of supports can be achieved by the reaction between AlCl_3 and the surface hydroxyl groups on the support and this is accompanied by HCl release [15,16]. Over 90% of the chloroaluminum species on the surface of the immobilized catalyst have a composition of $[-\text{O}-\text{AlCl}_2]$. Therefore, the different $[-\text{O}-\text{AlCl}_2]$ loadings on the SiO_2 and $\gamma\text{-Al}_2\text{O}_3$ supports can be attributed to different amounts of surface hydroxyl groups.

Table 1 shows the catalytic performance of the $\text{AlCl}_3/\text{SiO}_2$ catalyst for α -pinene isomerization at different temperatures. $\text{AlCl}_3/\text{SiO}_2$ gave high catalytic activity and the conversion of α -pinene increased significantly with an increase in the temperature. Almost 100% conversion of α -pinene was achieved at 60 °C for 30 min but the selectivity toward camphene and limonene decreased while the amount of high retention products increased. The reduction of limonene

indicated that limonene transformed into α - and γ -terpinene by consecutive reactions at relatively high temperatures (Scheme 1). Increasing the reaction time at a relatively low temperature (Fig. 1) resulted in an evident improvement in the conversion of α -pinene whereas selectivity toward camphene and limonene remained nearly constant. For example, 98.4% α -pinene conversion and 93.7% selectivity toward the main products were obtained when the reaction was carried out at 40 °C for 120 min.

Table 2 shows the catalytic performance of the $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst during α -pinene isomerization. $\text{AlCl}_3/\gamma\text{-Al}_2\text{O}_3$ gave much higher activity than $\text{AlCl}_3/\text{SiO}_2$. The 80.6% α -pinene conversion and 96.5% selectivity toward the main products were achieved when the reaction was carried out at 30 °C for 30 min. When the reaction temperature was raised to 45 °C, 100% α -pinene conversion was obtained and the selectivity toward the main products decreased slightly. Similarly, 95.5% α -pinene conversion and 94.4% selectivity toward the main products were achieved upon prolonging the reaction time at a relatively low temperature (Table 2, entry 4).

Studies on the surface acidity of the immobilized AlCl_3 catalyst indicated that large amounts of strong Lewis and Brönsted acid sites exist [17,18]. Özkan et al. [19] found that camphene and other bicyclic products were preferentially formed on Lewis acid sites while monocyclic products were preferentially formed on Brönsted acid sites and the distribution of products was related to the change in the Lewis/Brönsted ratio. Therefore, the high catalytic performance of the immobilized AlCl_3 catalyst in this work is due to the strong acidity.

In summary, an immobilized AlCl_3 catalyst is shown to be a novel environmentally friendly solid acid catalyst, which can catalyze the isomerization of α -pinene effectively. Further work will focus on the modification of the support to improve selectivity toward a single product by adjusting the Lewis/Brönsted ratio and this will provide an experimental basis for the transformation of turpentine into high-value products.

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