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γ-Al_2O_3 Supported SO_4^{2-}/ZrO_2 Solid Superacid Catalysts for n-Pentane Isomerization

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Abstract

A solid superacid catalyst Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ for n-pentane isomerization, was prepared by incipient-wetness impregnation. Preparetion conditions, namely, calcination temperature, concentration of sulfuric acid solution used in impregnation and Al_2O_3 concentration, were varied to investigate the effects on catalytic performance of Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$. The results showed that the PtSZA catalyst exhibited excellent catalytic performance for n-pentane isomerization. Under optimized preparation conditions of calcination temperature of 650˚C, reaction time for 3 h, concentration of sulfuric acid solution for 0.5 mol/L, 30% of Al_2O_3 concentration and 0.3% of Pt concentration, the n-pentane conversion and isopentane selectivity of Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ could reach up to 62.17% and 91.60%, respectively.

Keywords

SO_4^{2-}/ZrO_2, n-Pentane Isomerization, γ-Al_2O_3, Supported Superacid Catalysts

1. Introduction

The isomerization of light paraffins to branched isomers is an important process in refining industry, which has a wide range of applications in increasing gasoline octane number, reducing diesel oil solidifying point and improving low temperature property of lubricant base oil. Although the early light hydrocarbon isomerization cat-

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alyst (such as H_2SO_4 and HF) has high acid strength, it is strong corrosive and toxic. Therefore, it has been abandoned with the growing awareness of environmental protection and safety. At present, Chloride treatment of Pt-$A1_2O_3$ type low-temperature isomerization catalysts are widely used in the industry and usually have high activity and selectivity. The isomerization catalyst in the use process generally requires the addition of a small amount of chlorine to maintain catalytic activity. However, there are corrosion and pollution problems over the catalyst loading and handling process. It is sensitive to water, sulfur and thus raw materials are not allowed to contain water and sulfur, which limits the application of the process. In 1979, Hino and co-workers impregnated amorphous zirconium hydroxide with sul-furic acid to give upon calcination a solid superacid (Hammett acidity < −16) capable of catalyzing the isomerization of n-butane [1] [2]. The study on the SO_4^{2-}/ZrO_2 isomerization reaction for for n-butane at room temperature was performed by Hino, and SO_4^{2-}/ZrO_2 showed very high catalytic ctivity. Since then, SO_4^{2-}/ZrO_2 solid superacid catalysts caused extensive concern of the researchers. Compared with liquid acid catalysts, solid acid catalyst has the advantages of high catalytic efficiency, simple preparation method, easy separation of products, being non-corrosive, environmentally friendly and reusable. Solid super acid not only overcomes many disadvantages of liquid acid catalyst, but also presents high catalytic activity in many reactions of isomerization, alkylation, dehydration and esterification. However, from the view point of practice, the activity of SZ needs to be improved further, at the same time the use of isomerization catalysts can reduce costs. The task of decreasing its cost remains important and challenging. Some researchers [3] suggested that supporting sulfated zirconia on a cheaper porous material may be a good way to enhance the amount of superacid site by increasing the surface area and lowering the cost of catalysts.

By using solid superacid catalyst in light hydrocarbon isomerization process, the isomerization products are environmental gasoline harmonic components that do not contain aromatics and olefins. Moreover, the process itself is environmental as well, which overcomes the corrosion problem in the traditional low-temperature isomerization process. Hence, it has attracted increasingly attention from word-wide researchers [4].

2. Experiment

In this paper, the Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ catalyst was prepared by two step method. The n-pentane selected as reaction mediums for catalyst evaluation, and n-pentane isomerization performance of catalysts was evaluated in a 10ml fixed bed microreactor-chromatography unit with high pressure continuous flow. The catalyst was placed in the middle of the reactor while the rest empty volume was filled with quartz sand. The effect of different preparetion conditions on n-pentane isomerization performance of Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ was mainly investigated.

Chemical reagents: $ZrOCl_2{\cdot}8H_2O$ (analytical pure, Shanghai richjoint Chemical Reagent Co. Ltd.); single water of aluminum hydroxide (Fushun No.3 oil factory); n-pentane (analysis purity, Shenyang Huadong Reagent Factory); $H_2PtC1_6{\cdot}6H_2O$ (analytical pure, Shenyang Jinke Reagent Factory); sulfuric acid (analysis purity, Kunshan Jincheng Reagent Co. company); nitric acid (analysis purity, Kunshan Jincheng Reagent Co. Ltd.); concentrated ammonia solution (concentration 28%); silver nitrate solution (0.1 mol/L^{-1}); hydrogen (purity over 99%).

Preparation of catalyst: The catalyst was prepared as follows: The required amount of $ZrOCl_2{\cdot}8H_2O$ was dissolved in deionized water. Aqueous ammonia was added dropwise to a solution of $ZrOCl_2{\cdot}8H_2O$ until pH = 9 - 10, and then the precipitation was obtained. After being stored at room temperature for 24 h, the precipitation was washed repeatly with deionized water until the washing liquid is no longer able to check out the Cl^{-1} ion (0.1 mol/L^{-1} $AgNO_3$ solution). And then dried in oven (383 K, 24 h), the obtained powder was denoted as $Zr(OH)_4$ and grinded into less than 100 mesh. $Zr(OH)_4$ was mixed with proper amount of alumina. The obtained mixture immersed in sulfuric acid solution, dried at 383 K overnight then dipped $H_2PtC1_6{\cdot}6H_2O$ solution. After drying at 383 K overnight, suitable amount of sesbania powders and 18% dilute nitric acid solution were added. Followed by extruding forming, drying and calcining in muffle oven at given temperature is to obtain the Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ catalysts, denoted as PtSZA.

3. Results and Discussion

3.1. Effect of Calcination Temperatures on n-Pentane Isomerization Rate and Selectivity of Pt-SO_4^{2-}/ZrO_2-Al_2O_3 Catalyst

The effect of calcination temperatures on conversion of n-pentane isomerization reaction rate and selectivity is shown in **Figure 1**. As can be seen, calcination temperature is varied from 550˚C to 650˚C, the conversion of n-pentane and isopentane yield increases and maintains a high selectivity. Increasing the calcined temperature up to 700˚C, conversion of n-pentane and isopentane yield are obviously decreased. Although there is the decomposition and loss of SO_4^{2-}, the interaction of SO_4^{2-} with the catalyst surface is strong when the calcination temperature is below 650˚C. The most ZrO_2 exist mainly as tetragonal, monoclinic accounts for only a small proportion, thus the catalyst has high activity. After high temperature calcination rises up to 700˚C, most of SO_4^{2-} loss, sulfur content is very small and the average pore size of the catalyst becomes large, which resulting in very small specific surface area. And the thermally treated reduces the proportion of the ZrO_2 tetragonal and increases monoclinic crystal ratio, so leading to the decreasing activity of the catalyst for n-pentane isomerization.

3.2. Units Effect of Sulfuric Acid Concentrations on the Catalyst Performance

Figure 2 presents n-pentane isomerization performance for the Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ catalysts with different sulfuric acid concentrations. The experimental results show that solid superacid catalysts with superior performance must ensure to have the appropriate concentration of SO_4^{2-}. The relationship between SO_4^{2-} and ZrO_2 must achieve the best match with each other, so that we can get highly active and selective solid super acid catalysts.

This is because high concentration of H_2SO_4 forms the sulfate and then covers the part of the acid site. So that the problems caused by uneven distribution of the acid site will affect the activity and the selectivity of the reaction. When the H_2SO_4 concentration is 0.25 mol/L, under the same reaction conditions, the conversion of n-pentane and selectivity of the Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ catalysts are both lower than 0.5 mol/L. This shows that the number of acid active centers, formed by SO_4^{2-} and ZrO_2 on the catalyst surface, decreases with low H_2SO_4 concentration.

3.3. Effect of Al_2O_3 Contents on the Properties of Solid Superacid Catalyst

To clarify the influence of Al_2O_3 and ZrO_2 over properties of solid superacid catalysts, the Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ catalysts with different Al_2O_3 loading were prepared. The results on the isomerization reaction of n-pentane are summarized in **Figure 3**. The introduction of Al_2O_3 plays an important role in dispersing ZrO_2, and generates a synergistic effect of ZrO_2 and Al_2O_3. The grain growth of ZrO_2 is inhibited, so that the crystallization temperature increases. Since the tetragonal ZrO_2 to monoclinic transformation is inhibited, the specific surface area of the sample and sulfur amount of catalyst increasing, the catalyste acid enhancing and thus acid number is also a corresponding increase. These results are beneficial for producing strong acidity and enhancing catalytic activity. As can be seen from the **Figure 3**, when the Al_2O_3 content is more than 40%, the conversion rate of n-pentane

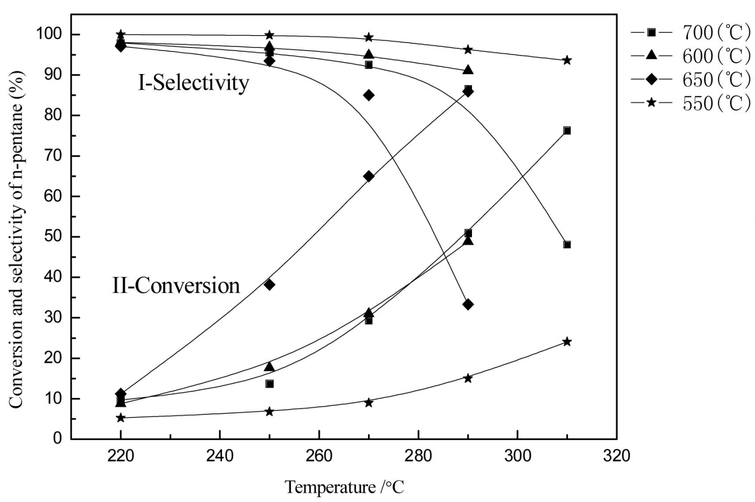

Figure 1. Effect of calcined temperature on n-pentane conversion or selectivity.

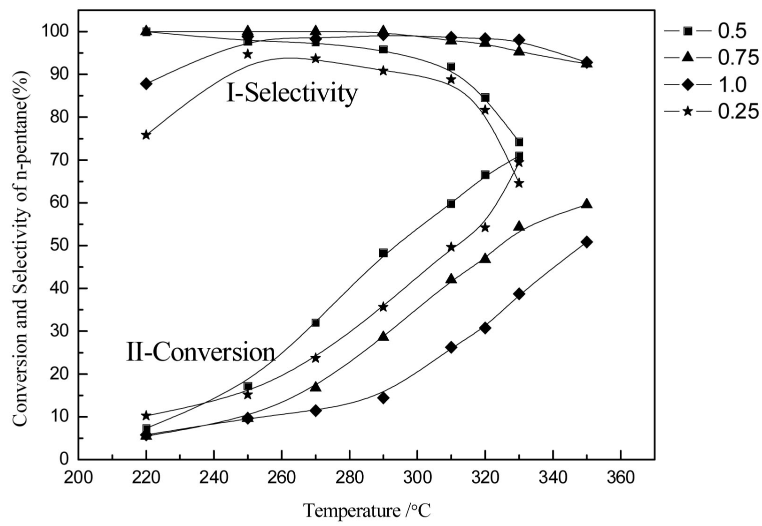

Figure 2. Effect of SO_4^{2-} concentration on n-pentane conversion and selectivity.

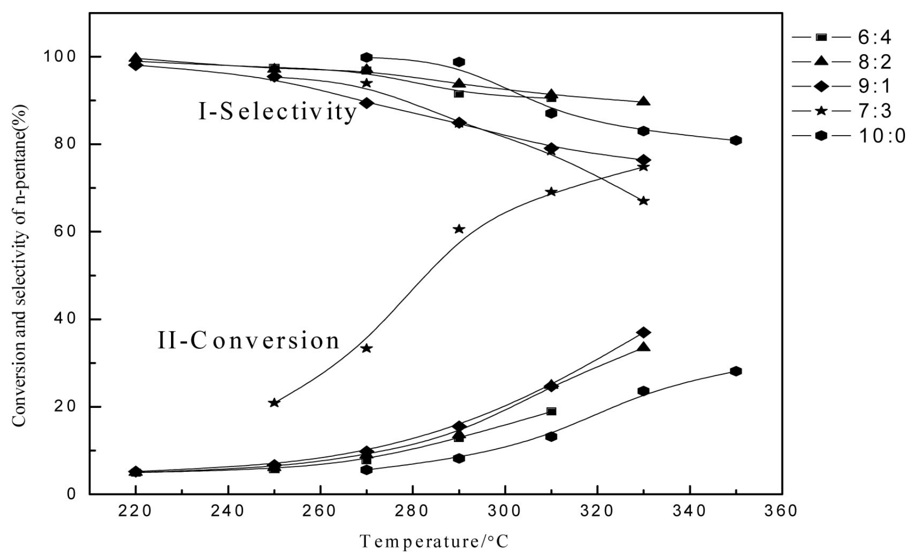

Figure 3. Effect of Al_2O_3 content on n-pentane conversion and selectivity.

declines. It indicates that forming strong acid centers should reduce the ZrO_2 content requiring. However, the number of the active center is reduced, leading to decreasing activity. Therefore, introducing the appropriate amount of Al_2O_3 can increase acid strength of the catalyst, so as to improve catalytic activity and stability of the Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ for n-pentane isomerization. **Figure 3** presents the n-pentane isomerization reaction for the Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ catalysts with different ZrO_2/Al_2O_3 ratios. Among all catalysts, it is clear that the catalyst shows the highest isomerization activity and selectivity while the ZrO_2/Al_2O_3 ratio is 7:3.

4. Conclusion

The best conditions for preparation of Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ solid super acid catalyst are determined by experiment. The results show that the optimal preparing conditions are 30% of Al_2O_3 mass fraction, impregnating with 0.5 mol/L H_2SO_4 solution, 0.3% of Pt mass fraction and calcining at 650˚C. The n-pentane conversion and isopentane selectivity of Pt-SO_4^{2-}/ZrO_2-$A1_2O_3$ could reach up to 62.17% and 91.60%, respectively. The catalyst is simple for preparing environment friendly and highly potential in industrial application.

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