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Research on Direct Epoxidation of Propylene on Modified Au/TS-1 Catalysts

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Abstract: Au/TS-1 catalyst was prepared by deposition-precipitation method. The catalytic performance of the modified catalyst for propylene direct vapour-phase epoxidation was investigated by modifying the support TS-1 and adding promoters during the preparation of the catalyst. Combined with the characterization results of X-ray powder diffraction (XRD), ultraviolet-visible diffuse reflectance (UV-Vis) and infrared diffuse reflectance (FT-IR), it was found that the activity of propylene epoxidation could be significantly improved by modified catalyst. The results showed that the catalyst modified by Sn increased the conversion of propylene and the selectivity of propylene oxide on the, which might be due to the coordination effect caused by the addition of Sn. The pore volume and specific surface area of Au/TS-1 have little effect on the vapour-phase epoxidation reaction, and the decomposition ability of Au/TS-1 is an important factor affecting its reactivity.

1. Introduction

Propylene epoxide is an important chemical raw material. It can react with nucleophilic substances in the presence of catalyst, and has a wide range of applications. At present, the methods of producing propylene epoxide are chlorohydrin, indirect oxidation and hydrogen peroxide oxidation. Chlorol method and indirect oxidation method belong to the traditional methods, which are prone to produce a large number of wastewater in the process of preparation, causing great pressure on the environment. Propylene oxide, also known as propylene oxide, methyl ethylene oxide, is a flammable, explosive and soluble in water, low boiling point and ether liquid. Propylene oxide is an important basic raw material for organic chemical synthesis. It is the third largest organic chemical product in propylene derivatives after polypropylene and acrylonitrile. Propylene oxide has two optical isomers, and its industrial products are racemic mixtures of two isomers.

Generally, TS-1 particles synthesized by the classical method are smaller than TS-1 particles and have better catalytic performance, but the price of TS-1 is expensive, which limits the use of TS-1 to some extent. The TS-1 particles obtained by using as template, ammonia or organic base as base materials are large, and have good catalytic activity in some reactions of TS-1. However, compared with TS-1 synthesized by classical method, the properties of TS-1 still lag behind, and there are some problems such as poor product reproducibility, low activity and selectivity in propylene vapor phase epoxidation. Modification was carried out to improve its reactivity. In the process of TS-1 synthesis, because the hydrolysis of Titanic vinegar inevitably produces precipitation and prevents titanium from entering the framework of molecular sieve, acid treatment is a common method to eliminate non-

skeletal titanium in TS-1 samples, but it can lead to partial removal of skeletal titanium species. Alkali modification is another common method to improve the catalytic oxidation activity and stability of TS-1 zeolite. Quaternary ammonium alkali and template were used to crystallize TS-1 samples twice, so that some non-skeletal titanium species were transformed into skeletal titanium species.

One-step epoxidation of propylene has the advantages of simple process, less by-products and environmental friendliness. It is the future development direction of the production process. Solid-phase catalyst production is a research hotspot. However, the conversion of propylene is generally low in the propylene epoxidation catalysts which have been studied extensively in previous years, and there is still a considerable distance from industrialization. In recent years, TS-1 catalyst has great competitiveness with one-step epoxidation of propylene, relatively good catalytic activity and selectivity, and has potential for industrialization. However, improving the conversion rate of propylene is still a key issue in the research of TS-1 catalyst system. In this work, TS-1 supported Au catalyst prepared by deposition and precipitation method was used as the research system to study its effect on propylene epoxidation. Aiming at the disadvantages of low conversion of propylene and poor stability of the catalyst, this study improved the catalytic performance of a catalyst by modifying the support. Meanwhile, the relationship between the catalytic performance and the structure and properties of the catalyst was studied by various characterization methods, and the important reaction mechanism of the catalyst was explored.

2. Direct epoxidation of propylene on modified Au/ TS-1 catalysts by Sn

2.1 Experiment

50mmolTEOS was added to dilute HCl solution with a concentration of 0.05mol_L-1 at a rate of 7s/drop. Then 1.5mmol TBOT was added to a certain amount of isopropanol (IPA). The IPA solution containing TBOT was mixed evenly. IPA solution containing TBOT was slowly added to dilute HC1 solution with TEOS at a rate of 7s/drop, and stirred up for 30 minutes under the condition of ice water bath. Clarified that the transparent mixed solution quickly added 2213.5mmolTPAOH (25wt% aqueous solution) and stirred vigorously. The solution gradually thickened, and finally turned into a milky white gel gel. Every time the 150ml deionized water was thoroughly cleaned, and the white powder solid dried in the vacuum oven at 60 degrees Celsius was put into the tube furnace at 3 degrees C /m. At the heating rate of in, the target product TS-1 molecular sieve the white colloid will be formed after dropping into the above-mentioned mixing solution. The white colloid in the beaker will be crushed by aging of the white colloid. The white solid powder is transferred to the white lining of the autoclave after overnight drying in the electrothermal constant temperature blast dryer. The solid powder is added according to the mass ratio, stirred evenly, and then crystallized. The carrier TS-1 was synthesized in the same way, only adding a certain proportion of n-butyltin diluted with n-heptane in the isopropanol solution, and then slowly dropping the mixture into the mixture in proportion, the other steps were the same.

2.2 Characterization of UV-Vis carrier

Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) is an effective method to characterize the presence of Qin in molecular sieves. Fig. 1 is a spectrogram of TS-1 with different Sn dopants. The sample shows only a strong absorption peak at the site, which can be attributed to the electron transition from the bonding-assisted orbital of skeletal oxygen to the tetra-coordinated skeletal Qin-Sky orbital. It is an important evidence of entering the molecular sieve skeleton. There is no absorption peak at this point, indicating that there is no crystalline phase. The addition of Sn has no obvious effect on UV-Vis spectra, which may be due to the small amount of Sn. TS-1 and solvent form stable five-membered ring transition state through hydrogen bonding. The oxygen atom in the five-membered ring provides a pair of electrons when it is double bonded with the coordination. It has certain electrophilicity and reacts with propylene to form a stable five-membered ring transition state. The mechanism can better explain the solvent effect. Propylene epoxidation in alcoholic solvents is

more active than in other solvents because proton solvents can coordinate with peroxide to form stable quintuple transition state, which increases the stability and electrophilicity of TS-1. At the same time, because the narrow pore of TS-1 can produce steric hindrance effect, the activity of propylene epoxidation in methanol is higher than that in other alcohols. Hydrogen peroxide is formed on the surface of gold by hydrogen and oxygen, and then reacts on the active centre. It is pointed out that this reaction mode has the lowest energy barrier.
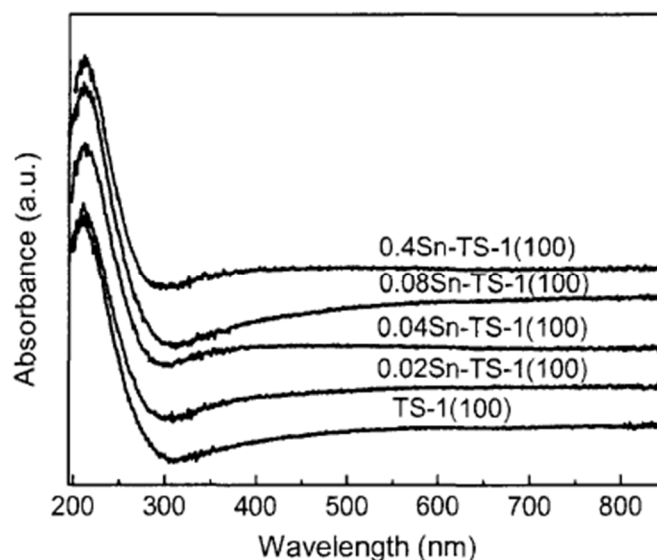

Figure 1. UV-Vis spectra of various TS-1 samples

2.3 XRD analysis of catalyser

Figure 2 shows that the synthesized TS-1 sample has a typical structure and good crystallinity. The diffraction peak of Au is not seen in the diagram, indicating that gold particles are highly dispersed on the carrier. It can be seen from Fig. 2B that the characteristic diffraction peak shifts to a small angle when Sn is doped into the TS-1 carrier, because the ionic radius is larger than the ionic radius, the lattice may expand after entering the molecular sieve skeleton, so that the lattice parameters become larger. The results of XRD clearly showed that the framework of TS-1 zeolite was replaced and some Si was replaced. Deactivation is an unavoidable problem for the catalyst system. For the catalyst, the catalytic activity decreased after the reaction. What is more serious is that it will lose itself. The deactivation is due to the acidity of the catalyst surface and the accumulation of disproportionation products. The catalyst can be regenerated in an oxygen atmosphere. Recent studies further show that the catalyst has good stability under reaction conditions. The properties of different epoxidation of gold (mass fraction and different catalysts) were discussed. The results showed that the catalyst had a high ratio and a low content of gold, and showed very good stability. There was no deactivation of the catalyst in the evaluation. If the content of high gold is used, the activity of the lower mass fraction will decrease after reaching the maximum value. Therefore, the deposition of highly dispersed gold and gold is necessary for the stability of the catalyst.
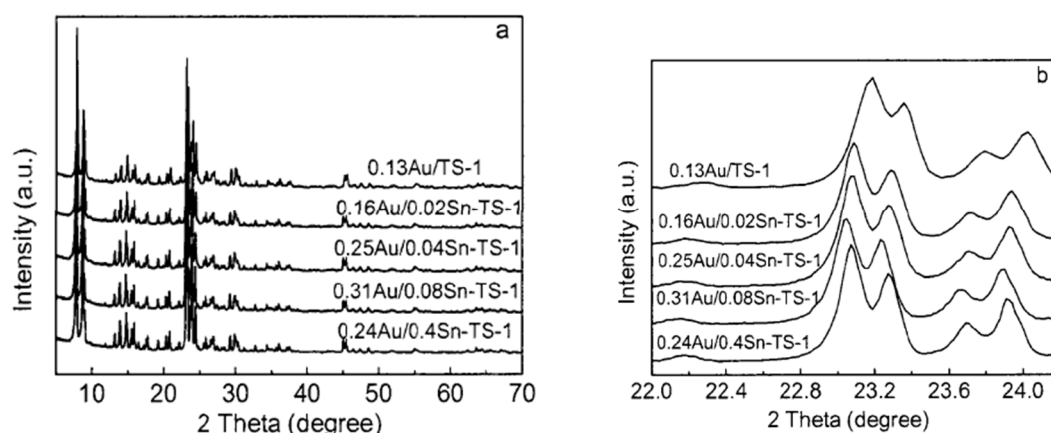
Figure 2. XRD patterns of catalysts with different Sn contents

2.4 FT-IR analysis of catalyser

Figure 3 is the FT-IR spectrum of each catalyst. It can be seen that the peak at 550 cm-1 belongs to the characteristic absorption peak of the five-member ring of the secondary structure unit of TS-1 molecular sieve skeleton. The peak at 1100 cm is caused by the antisymmetric stretching vibration of the four-dimensional units in the inner S C. The peak at 1230 cm-1 is caused by the vibration of the external connection of the molecular sieve. These absorption peaks also prove me. The synthesized TS-1 has MFI structure. The peak at 960cm-1 is the characteristic fingerprint peak of titanium entering the framework of molecular sieve. The characteristic peak shifted to 970 cm-1 when Sn was added to the support. The molecular catalytic system was the most concerned in the catalytic epoxidation of propylene. The advantage of this method is that as an environmentally friendly oxygen source, it can be used to epoxidation of propylene with high selectivity and high efficiency under the condition of mild, simple and non-polluting conditions. It is stable in nature, easy to recycle, and can be recycled, but the disadvantage is that EPO itself is a cheap chemical products, and as an oxygen source to produce EPO C is expensive, economically uneconomical, and the storage and transportation links have security risks; in addition, because the synthetic molecules need to be expensive. Precious tetra propyl ammonium oxide as a template, making its own high price, so far has not been industrialized.
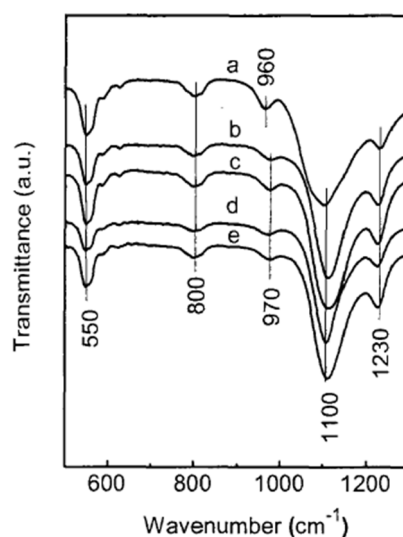

Figure 3. FT-IR analysis of catalyser

3. Direct epoxidation of propylene on modified Au/ TS-1 catalysts by Na₂SO₃

3.1 The effect of Na₂SO₃ quality on propylene conversion

Gas phase epoxidation of propylene with AuTS-1 before and after isovolumetric impregnation and several solution modifications was carried out respectively. The results showed that the propylene conversion and selectivity of propylene oxide of AuTS-1 before and after modification were sum, respectively. After solution modification, the propylene conversion was slightly reduced, but the selectivity of propylene oxide was zero. After isovolumetric impregnation modification, the conversion of propylene and selectivity of propylene oxide were increased to 6537 Mesoporous materials these two isotherms show sharp changes in the relative pressure range of 0.20 0.35, which is characteristic of capillary condensation in mesoporous materials. This means that these samples have typical pore and macro pore volumes with uniform structural size distribution At the same time, the obvious hysteresis loops at the relative pressure of about 0.9 may be caused by The adsorption and desorption curves of N_2 on the secondary mesoporous capillary condensation TS-1 zeolite support increase sharply at relative pressure. The shape of N_2 adsorption and desorption curves is type I. It is a typical microporous zeolite material. The maximum absorption peak of Na_2SO_3 is located at about 225 nm, the maximum absorption peak of TS-1 is located at about 210_nm, and the maximum absorption peak is slightly offset due to distortion. In addition, there is a moderate absorption peak at 270 nm and a weak absorption peak at 330 nm. These two peaks are the characteristic absorption peaks of amorphous TiO_2 and anatine TiO_2, respectively.
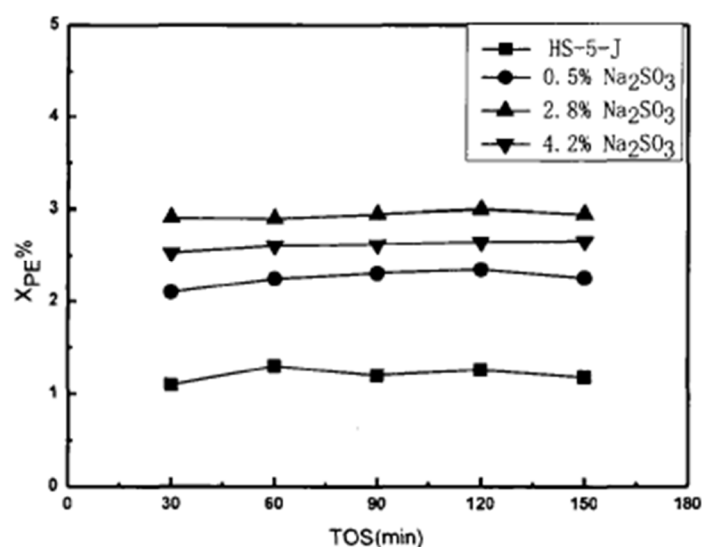

Figure 4. The effect of Na2SO3 quality on propylene conversion

3.2 The effect of Na₂SO₃ quality on propylene selectivity

The isovolumetric impregnation treatment with different amount of Na_2SO_3 can improve the one-to-one gas-solid epoxidation activity, and the optimum amount of modifier Na_2SO_3 can make the conversion of propylene 3.0% and the selectivity of propylene oxide 76%. The above conclusions clearly distinguish the Ti species in the three Ti-containing zeolite carriers, especially the matrix Ti. The coordination environment of the molecule sieves includes defective or distorted skeleton Ti atoms, and the TS-1 molecular sieves mainly contain fully tetra-coordinated skeleton Ti atoms. Moreover, we can believe that we have successfully synthesized hybrid AuTS-1 molecular sieves with microporous structure by using TS-1 seed solution because of the existence of microporous structure in the hybrid AuTS-1 molecular sieves. Compared with conventional zeolites, AuTS-1 has larger specific surface

area and pore volume, and smaller pore size. Meanwhile, the coordination of Ti in the framework of hybrid AuTS-1 zeolites should be between the zeolite and TS-1 zeolite. The solution of Au precursor used in the process of loading nano-gold particles onto Ti-bearing carriers by sedimentation precipitation method should be the same. The concentration of Au on the three nano-gold catalysts is the same, but the load of Au on the final three nano-gold catalysts is very different. The specific load of Au on the catalysts is characterized by ICP-AES. The actual load of Au on Au/TS-1 catalyst is 0.25%, and that on AuTS-1 catalyst is about 1.3%, which is much higher than that on Au/TS-1 catalyst. Intermediate Au loading In the process of preparing gold nanoparticles by DP method, the final actual Au loading depends on the value of the support used.
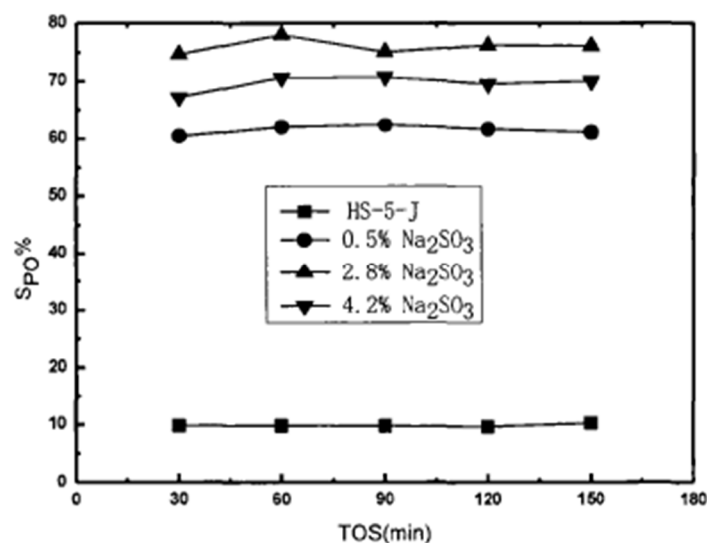

Figure 5. The effect of Na_2SO_3 quality on propylene selectivity

3.3 The effect of Na_2SO_3 quality on propylene temperature

The pore volume and specific surface area of AUTS-1 before and after sodium modification are shown in the following table. From the surface, it can be seen that the pore volume of the sample before and after modification is basically the same, and the specific surface area of the sample decreases, especially for the sample impregnated at 20 C. The TS-1 catalyst with commercial potential is very low in load. It did not find nano-sized particles, suggesting that the catalytic activity depends mainly on the smaller invisible clusters. Therefore, the TS-1 catalyst loaded with TS-1 has catalytic activity for the direct epoxidation of propylene, and the TS-1 catalyst loaded with invisible clusters in the TS-1 pore, and the TS-1 catalyst loaded with nano-sized particles visible on the surface of the TS-1 catalyst with higher loading are active for the direct epoxidation of propylene. In the same TS-1 literature, the authors synthesized a series of TS-1, which were supported on TS-1 by deposition precipitation method. When the concentration of the deposition solution was the same, the loading amount on the catalyst depended on the concentration of the deposition solution, which could increase the loading amount on the catalyst, but the activity, selectivity and stability decreased. These findings suggest that small particles may preferentially deposit around the site, and that the number of TS-1 active sites is likely to have an optimal TS-1 value when the content is fixed. The gold catalyst prepared by deposition and precipitation method is the key to increase the active site concentration of the catalyst. Increasing the concentration of the deposition solution can increase the loading on the carrier, but it can reduce the direct epoxidation activity of propylene. It can remarkably increase the gold capture ratio deposited on the support to gold in precursor acid and the catalytic activity of TS-1 catalyst for propylene epoxidation. The average capture rate of gold is several times higher than that without pre-

treatment. The increase of capture rate indicates that it is possible to obtain the same amount of catalyst with lower concentration of acid precursor.

Table 1. The effect of Na_2SO_3 quality on propylene temperature

Sample	v_p (ml/g)	$S_{BET}(m^2.g)$
AUST-1	1.18	382
20 degrees Celsius	1.17	396
50 degrees Celsius	1.19	325
80 degrees Celsius	1.14	381

4. Conclusions

In view of the low activity and stability of the catalyst for propylene epoxidation on AuTS-1, the addition of other transition metal elements was studied. The results show that the addition of Sn decreases the catalytic activity, but the conversion of propylene increases. The effect of Sn on the performance and structure of the catalyst needs further study. However, the conversion of propylene and the selective addition of noble metals keep certain stability in the reaction process, which improves the conversion of propylene.

Acknowledgement

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