Research on Gas-Phase Direct Epoxidation of Propylene by Nanosized Gold Catalysts

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Abstract: One-step synthesis of propylene oxide from propylene in gas phase in the presence of hydrogen and oxygen is an environmentally friendly and energy-saving ideal reaction, which has important research value. The gold catalyst prepared by deposition and precipitation method has the advantages of small particle size, high dispersity and good activity. It is used for epoxidation of propylene in gas phase. The selectivity meets the requirements of industrialization. However, how to improve the conversion of propylene is still the focus of research. The effect of doping on the gas phase epoxidation of propylene is obvious. The purpose of this paper is to synthesize titanium silicate molecular sieves with composite structure and corresponding nano-gold catalysts by combining the advantages of high stability, weak surface acidity, large specific surface area, large pore size and pore volume of microporous titanium cinnamon molecular sieves.

1. Introduction
At present, the main methods of PO production in industry are chlorohydrin method and peroxide method, but chlorohydrin method will produce many chlorine-containing wastewaters in the process of production, and the environmental pollution is very serious; while peroxide method has the disadvantages of producing many by-products in the production process, low selectivity, and large investment in equipment. At present, the production of PO by chlorohydrin is widely used in industry in China. The environmental pollution caused by this process cannot be ignored. Therefore, it is always the goal of all circles to develop a direct epoxidation method for PO production from propylene with friendly environment, low energy consumption and high selectivity to the target product. Hydrogen peroxide liquid-phase epoxidation of propylene to PO has the advantages of environmental friendliness, mild reaction conditions and high selectivity to the target product PO. It is generally considered to be a new green process to replace the existing PO production process. However, H2O2 is difficult to store and transport and its price is high, which makes the process green.

In 1998, Haruta et al. discovered for the first time that nano-gold catalysts supported on TiO2 could catalyse the vapor phase epoxidation of propylene in the presence of H2. It was found that the nano-gold catalysts prepared by deposition-precipitation method with various TiO2 and various mesoporous.

Chlorohydrin method has a long history and has been industrialized for many years, representing enterprises as Dow Chemical Corporation. The chlorohydrin process includes chlorohydrin and product separation. The traditional chlorohydrin method mainly uses lime as the raw material for oxidation. In recent years, with the emergence of more and more improved industrial production
methods of chlorohydrin method, more and more factories have adopted the advanced method of raw materials mainly composed of electrolyte. It is a process in which propylene, chlorine and water are injected into a bubbling tower tubular reactor without internal components to produce chlorohydrin at about one atmospheric pressure. The conversion of propylene is achieved, and chlorine in the reaction is almost completely transformed. The by-products are mainly two chlorpromazine and two chloropropyl ether. The company adopted the method of combining chlor-alkali unit with chlorohydrin process unit to replace the lime in the oxidation process of traditional method. This improved chlorohydrin process produces chlorine which is involved in the reaction of synthesizing chloropropene under the action of electrolysis, which is contained in the electrolyte, then saponified with chloropropene, and finally formed. At present, chlorohydrin method is still used in the domestic production capacity of epoxy propylene besides the co-oxidation method used in the CCS Shell Epoxy Propylene Plant. Developed countries such as Europe and the United States have already phased out the backward chlorohydrin process. Therefore, it is imperative to find other effective and green production methods as soon as possible while actively developing the polypropylene industry in China.

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

2.1 Experiment
Take a large beaker 500 mL, put HCL in it, at room temperature magnetic stirring with a drop funnel drop of tetraethyl valerate: take titanic acid butyl vinegar added to isopropanol. Take a small beaker, first call isopropanol, then balance zero, and then call it acid. After dropping, we continue to stir and weigh the aqueous solution of oxy-money. We add it to the step by dropping and stirring it with a rubber-tip dropper. To the high-pressure reaction stick, according to the proportion of solid, while stirring dripping, and then with steaming water on the glass stick adhered to the precursor washed into high-pressure pan, catalpa into the oven 175 degrees crystallization, which will be put in high-pressure and then poured into a centrifugal cup, centrifugal three times. After the centrifugation is finished, wash the centrifuge cup with the steaming water and transfer to the clean beaker and dry. The dried solids were transferred to tree hazards and then heated to 500 C by temperature programmed roasting, resulting in TS-1. Like the above, the modified preparation was convenient. In the first step, a certain amount of the mixed solution was added and then slowly dripped into the mixed solution. The other steps were the same as the preparation. The carrier was named Ga-TS-1.

It was synthesized by using tetraethyl orthosilicate as silicon source and titanium source, cetyltrimethylammonium ammonium bromide and tetra propylammonium hydroxide (TPAOH) as template. The precursor solution containing TS-1 seed was first prepared by dropping 1.5mmol n-butyl titanate (TBOT) into a certain amount of isopropanol (IPA) solution. The clear and transparent mixed solution was added slowly to 50 mmol TEOS at a rate of 7 s/drop. The mixture was stirred vigorously for 30 min, dripped slowly into the above mixed solution under the condition of ice water bath for 13.5mmol TPAOH (25wt%) and put into the oven for 3 h. The clear and transparent solution was then cooled to room temperature. Ti-MCM-41-H zeolite was prepared by using TS-1 seed solution, which contained TS-1 microporous structure unit. It was stirred evenly to obtain milky white solution. TS-1 seed solution was added to the milky white solution at a rate of 7 s/drop while stirring vigorously. Then the reactants were fully stirred for 24 h. Then the reactants were transferred to the PTFE high-pressure reactor and placed in the oven at 100 degrees. The product of hydrothermal reaction of C for 24h was centrifuged and filtered, thoroughly cleaned with deionized water, and then dried overnight in vacuum oven at room temperature. The white powder solids were baked in tubular oven at 540 C for 4H at a heating rate of 1 C/min. The target product Ti-MCM-41-H molecular sieve was obtained.

2.2 Characterization of UV-Vis carrier
Figure is a spectrogram of the catalyst with different Ga content. This method can effectively detect the existence state of iron species in the molecular hoof. It can be seen from the diagram that the
catalysts doped with different content of Ga have strong absorption peaks, which can be attributed to the four coordination iron species entering the framework. No absorption peaks were found at each catalyst site, indicating that there was no crystalline phase in the catalyst. This may be because the amount of incorporation is very small, so it has no obvious effect on the UV-Vis spectrum of the sample. The N2 adsorption and desorption curves of the samples showed obvious hysteresis loops. The shape of the adsorption and desorption curves was IUPAC type IV and H1 type hysteresis loops, indicating that the two carriers were typical mesoporous materials. At the same time, the obvious hysteresis loops appearing at the relative pressure may be due to the N2 adsorption-desorption curve of the secondary mesoporous capillary condensation (TS-1) molecular sieve carrier, which has a sudden increase in adsorption capacity at relative pressure, and is a typical microporous molecular sieve material. The related structural characterization and elemental analysis of titanium silicate molecular sieves are used to characterize the modified or modified titanium silicate molecular sieves and the corresponding nano-gold catalysts, and further guide the adjustment of various preparation parameters. The titanium silicate molecular sieves with composite structure must have the following structural characteristics: large specific surface area, large pore size and regular pore size distribution, including more titanium defect sites and weak surface acidity. All these structural characteristics are prerequisites and guarantee for the preparation of highly active and highly stable gold nanoparticles catalysts.

Figure 1. UV-Vis spectra of Au/TS-1 catalysts with different Ga contents

2.3 XRD analysis of catalyser

Figure 2 is a map of adding different contents of catalyst. It can be seen from the graph that there are obvious characteristic diffraction peaks, which can be attributed to the characteristic diffraction of the samples with typical structure and good crystallinity. Propylene epoxidation on gold nanoparticles and its in-situ characterization. The gold nanoparticles were loaded on the Ti-containing supports and propylene epoxidation was carried out. The different reaction behaviours of the catalysts were

3
compared. At the same time, the effects of pore structure and Ti species chemical state on the adsorption and desorption behaviour of propylene were studied by kinetics and in situ characterization. On the other hand, the microscopic reaction mechanism is elucidated by derivation of kinetic parameters. Although the specific mechanism of deactivation of gold catalysts is still difficult to determine, the results show that the main reason for deactivation of the catalysts is that the side reaction of ring opening occurs on the surface of the catalysts, and the yield of PO in the reaction system is very low. When TS-1 catalysed propylene epoxidation, a small amount of neutral or acidic sodium salt was added to the catalyst to neutralize the acidity of the catalyst surface. It was found that TS-1 could significantly inhibit the ring opening reaction, but had no effect on the epoxidation performance of propylene. Therefore, in the future research, the open-ring reaction of PO can be inhibited by adjusting the properties of acidic sites on the surface of the catalysts, and the deactivation of the catalysts can be delayed while increasing the yield.
2.4 Characterization of NH3-TPD

Figure 3 is the NH3-TPD diagram of the catalyst modified by different Ga content. It can be seen from the diagram that the desorption peak of NH3 shifts to low temperature with the addition of Ga, indicating that the acid strength of the catalyst decreases with the addition of Ga. The peak area of desorption increased with the increase of doping amount, which indicated that the number of acid centres on the catalyst surface increased. During the epoxidation of propylene, monodentate proxy species are formed by the ring opening of PO molecules adsorbed on the reaction centre, which further interact with the adjacent epoxidation centres to form bidentate species, resulting in the reduction of epoxidation active centres and the decrease of epoxidation activity. Similar explanations are also applicable to gold catalysts supported on TS-1 zeolite. In situ infrared spectroscopy was used to study the epoxidation of propylene on the surface of gold catalysts. It is suggested that the deactivation of the catalyst may be since the bidentate proxy species formed by the ring opening of PO molecules occupy the active centre of the reaction.
3. Discussion on modified Au/ TS-1 catalysts by nanosized gold catalysts

3.1 Au/La catalyst
Carrier La is prepared. 100 mL chloroaauric acid solution is put into a beaker. The carrier La is heated and stirred dropwise until it is close to the carrier. The temperature is kept cool after down stirring, centrifugal washing and vacuum drying with rotary evaporator. The obtained catalysts were recorded as Au/La. A series of catalysts with La were added, and the modified catalysts were selectively compared. For the modified catalyst, the tendency of decreasing propylene conversion and selectivity is not great, but the added catalyst. The trend of catalyst conversion and selectivity decreased obviously. If we continue to study the carriers of species, we believe that reasonable results will be obtained. The use of CsOH instead of NaOH as precipitant in the process cannot improve the utilization of H₂. The possible reason is that the basicity of CsOH is weaker than that of NaOH, which hinders the formation of active Au species. The addition of Ba(NO₃)₂ as promoter in Au-Ti catalyst can also improve the conversion of propylene. The reason is that the addition of Ba(NO₃)₂ decreases the surface acidity of the catalyst and facilitates the formation of intermediate species of hydrogen peroxide on its surface.
3.2 Au/Co-TS-1 catalyst
We mixed cobalt into Au/TS-1 and gold to form Au-Co alloy. The reaction rate of PO can reach 54gpo/h/kgcat at 120 OC. The utilization rate of H2 can reach 17%. We added cobalt to the carrier TS-1, hoping to improve the activity of the catalyst. The comparison of the activity of the catalyst with different Co loading capacity and the activity of catalyst without Co addition is given. From the activity evaluation diagram, the conversion of lactone is only 32%, 2, 6% and 2.2%, and the selectivity of propylene oxide is 82%, 50% and 77% respectively when the content of Co is 0.25g, 0.33g and 0.42g, respectively. After adding 0.33g Co, the selectivity of propylene oxide is not stable, which is of little significance. Compared with the conversion rate of propylene. For the selective effect of epoxy lactone, the selectivity of epoxy propane before modification without adding Co. Although it did not get the desired results, this did not mean that Co could not improve the catalytic performance of the system. The comparison of the activity of Co supported catalysts at different reaction temperatures is given. It can be seen from the diagram that when the loading is 042g, the conversion of inner is 0.75% and propylene oxide is 95% at 120 C, which is higher than that at 70 C. The yield of PO is also higher at low temperature. Compared with the conversion of propylene, the conversion of propylene is like that of propylene. The conversion of olefins before modification. If we improve the experimental conditions and reaction temperature, we believe we can get better results.
Figure 5. Epoxidation of propylene of catalysts with different Co contents

3.3 Au/NaOH catalyst

Figure 6. Epoxidation of propylene of catalysts with different NaOH contents

Figure 6 is the result of the reaction of NaOH treated carrier for propylene epoxidation of gold catalyst. It can be seen from the diagram that the conversion of endzone is 2% after treating TS-13 with 2M/L NaOH, 0.15% after treating TS-13 with 0.2M/L NaOH, and 0.05% after treating TS-11 with 0.1M/L NaOH. The conversion of propylene after liquid NaOH treatment is 0.46% lower. From the selectivity diagram of propylene oxide, we can see that the selectivity of propylene oxide is 10% after treating TS-13 with 2M/L NaOH, 70% after treating TS-13 with 0.2M/L NaOH, and 70% after treating TS-11 with 0.1M/L NaOH. The selectivity is about 67%.
4. Conclusions
Titanium silicate molecular sieve is a pot-supported gold catalyst for Direct Vapor-Phase epoxidation of propylene to propylene oxide. The catalyst has high activity and selectivity for PO. However, the problems such as low efficiency of hydrogen, safety of hydrogen-oxygen mixture, deactivation of gold catalyst and separation of PO need to be solved urgently. To improve the activity and stability of the catalyst, we try to add different elements during the preparation of the catalyst. The incorporation of La did not achieve good results. According to the literature reports, the experiment conditions need to be further optimized, and the treatment of NaOH has not achieved the desired results.

Acknowledgement
This work has been supported by Natural Science Foundation of China with grant No. 21506170 and 51602253.

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