Utilization of CO2 for production of aromatics via ZnO/ZrO2-ZSM-5 tandem catalyst.

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ABSTRACT

CO_2 Hydrogenation to Aromatics Tandem Catalyst Methanol Synthesis in Oxides Arene-Based Cyclization Over the past decades, great progress has been made in CO_2 hydrogenation to a variety of C1 chemicals, lower olefins, and gasoline. However, due to the extreme inertness and high aromatization barrier of CO_2, the synthesis of aromatics from one-shot CO_2 hydrogenation is still a major challenge. Here, we present a tandem catalyst consisting of ZnO/ZrO_2 and ZSM-5 zeolite for one-shot conversion of CO_2 to aromatics with 70% selectivity, and the selectivity of incoming methane is suppressed to below 1%. The path of $CO_2 \rightarrow CH_3OH \rightarrow$ aromatics over the tandem catalyst was demonstrated.

Keywords: Hydrogenation, polymer, methanol, catalyst

Enter. Although the use of fossil fuels has helped the development of human civilization, the huge emission of CO_2 has caused serious environmental problems. Therefore, the control of CO_2 emissions has become one of the main problems of the 21st century, and there is an urgent need to mitigate its negative impact on the environment. Catalytic CO_2 conversion is one of the promising approaches as it offers a sustainable approach for the production of fuels and chemicals, as well as helping to reduce dependence on non-renewable energy sources. In recent decades, considerable effort has been devoted to the development of efficient technologies for the production of various C1 products, such as CO_2 hydrogenation [1–7], methane [8–10], methanol [11–16], carbon monoxide [17] . formic acid [18].

Recent progress has also been made in the hydrogenation of CO_2 to liquid fuels [19,20] and lower olefins [21,22], which increases the limit of CO_2 utilization. Aromatic substances are mainly used for the production of polymers, which account for one third of the commodity petrochemical market. The global demand for benzene derivatives, polyester fibers and resins is growing at a rate of 6% per year.

In the current chemical industry, the production of aromatics relies mainly on oil. The depletion of oil and the gap between supply and demand require a new strategy to synthesize aromatics from alternative carbon sources [23–29]. A one-shot conversion of CO_2 to aromatics via a methanol intermediate is a promising way to address the "3R" (reduce, reuse and recycle) challenge of ever-increasing CO_2 levels, as well as to address the supply-demand conflict is aromatic substances, which creates a winning scheme.

The conversion of CO_2 to methanol is thermodynamically favorable at high pressure and low temperature (473-573 K), while the reaction from methanol to aromatics (MTA) usually requires low pressure (atmospheric) and high temperature (673-823 K). Therefore, the one-shot conversion of CO_2 to aromatics helps to avoid complex process design in a two-step process that operates separately from CO_2 to methanol and MTA.

It can also thermodynamically change the equilibrium conversion of CO_2 [30]. Metal catalysts (Pd, Au, Cu, etc.) are highly active catalysts for the production of methanol from CO_2 [31-33]. Recently, researchers found that metal oxides (In2O3, Ga2O3, etc.) also have high activity [13,34,35].

It should be noted that metal oxides often show methanol selectivity at high temperatures, which allows MTA to synthesize methanol under favorable reaction conditions. Zeolite ZSM-5 is beneficial in providing homogeneous active sites, uniform pore structure, precise acid strength and adjustable acid content, and it is able to catalyze the carbon chain growth reaction from methanol to hydrocarbons (MTH) [36–39]].

Therefore, to solve the problem of one-shot CO2 hydrogenation to aromatics, our strategy is to develop a tandem catalytic system consisting of metal oxide and zeolite, in which the CO2 activation and CeC coupling reaction can occur sequentially at two different types of active sites. . with CH3OH as an intermediate for chain growth. Such a design of the reaction pathway is useful for precise alignment of two independent active sites and highly selective production of target products by the shape-selective effect of zeolite channels.

With this strategy, we selected ZnO with unique hydrogenation ability and controllable density of surface hydrogen species as an active component for methanol synthesis [23,40] In addition, the oxygen storage capacity of the oxide support is also improved by small oxygen species such as CO_2, CO, and H_2O. related to the activation of z-containing molecules [34,35,41-43] In this context, ZrO2, which has a suitable oxygen storage capacity, has been chosen to facilitate the adsorption and activation of CO_2 [10,15,44].

Therefore, the ZnO/ZrO_2 catalyst was selected for the synthesis of methanol from CO2 hydrogenation at high temperature, where it is convenient to associate with the MTA reaction and can inhibit the formation of side products and the secondary hydrogenation of low-carbon olefins [15,23] In this work, we used CO_2 ~70 We have successfully constructed a ZnO/ZrO_2-ZSM-5 tandem catalyst for hydrogenation to aromatics with % selectivity. The effects of reaction conditions and zeolite acidity on the catalytic performance were studied in detail. The present work sheds light on the rational design of tandem catalysts to control activity and selectivity, opening a new way to utilize CO_2 through a previously inaccessible route.

2. Experimental part.

2.1. Preparation of catalysts.

2.1.1. Synthesis of ZnO/ZrO_2.

ZnO/ZrO_2 was synthesized by initial wet impregnation method. First, the supporting zirconia was impregnated with an aqueous solution of Zn(NO3) 2·6H_2O. After drying overnight at 373 K, the product was calcined in static air at 673 K for 6 h. The resulting catalyst was designated as ZnO/ZrO_2.

2.1.2. Synthesis of nano-sized S-1 crystal seed.

Nanoscale Silicalite-1 (S-1) crystalline seed was prepared by hydrothermal method, with tetraethoxysilane (TEOS, analytical reagent (AR)), tetrapropylammonium hydroxide (TPAOH, sodium and potassium less) as silicon source. more than 5 ppm) was used as a template and sodium hydroxide (NaOH, AR) was used as a base. The molar composition was 1.000TEOS:0.172TPAOH:0.008NaOH:30.420H2O. After stirring at 308 K for 6 h, the mixture was placed in a Teflon-lined stainless steel autoclave at 373 K for 3 days. The resulting solution was used for the synthesis of ZSM-5 without further processing.

2.1.3. Synthesis of Z5-AT.

ZSM-5 was prepared by the hydrothermal method, using silica (30 wt) as a silicon source, Al2 (SO4) 3·18H2O as an aluminum source, nanoscale S-1 crystal and sodium hydroxide (NaOH) as a template. as a basis. Typically, 1.90 g of NaOH is mixed with a solution of 50.8 mL of deionized water and 1.59 g of Al2(SO4)3·18H2O and the resulting mixture is stirred at 308 K for 5 min, then 5.10 g is added as -synthesized nano-sized S-1 crystal seed solution.

The above mixture was stirred at 308 K for 5 min and after addition of 12.75 g of silica (30 wt%) for another 4 h. The mixture was placed in a Teflon-lined stainless steel autoclave at 483 K for 6 h. The zeolite product was filtered and thoroughly washed with deionized water, dried at 373 K for 10 h. The template was removed by static air calcination at 813 K for 6 h. ZSM-5 was obtained by ion exchange with 1.0 M NH_4NO_3 solution at 353 K for 2 h. The product is filtered and thoroughly washed with deionized water, dried at 373 K for 10 hours. The product was calcined in static air at a temperature of 813 K for 4 hours, henceforth referred to as Z5.

Alkali treated ZSM-5 was prepared by treating Z5 with 0.6 M NaOH solution at 353 K for 1 h. The product was washed with deionized water until it became neutral, and Z5-AT was obtained by ion exchange corresponding to the ion exchange process of ZSM-5.

2.1.4. Z5-x synthesis.

ZSM-5 with different aluminum content was prepared using TEOS as silicon source and $Al(NO_3)_3·9H_2O$ as aluminum source; Tetrapropylammonium hydroxide (TPAOH, 1.2 M) was used as template and base. The molar composition of the mixture was 1TEOS: 0.27TPAOH: nAl_2O_3: $67H_2O$ ($n = 0.005$, 0.00167, 0.00125, 0.000833 and 0.000625). After stirring at 308 K for 6 h, the mixture was placed in a Teflon-lined stainless steel autoclave at 443 K for 3 days. The zeolite product is filtered and thoroughly washed with deionized water, dried at 373 K for 10 hours. Z5-100, Z5-300, Z5-400, Z5-600 and Z5-800 were obtained by calcination in static air at a temperature of 813 K for 6 hours.

Z5-50 was prepared by a similar method to that described above, and the molar composition of the mixture was 1TEOS: 0.47TPAOH: $0.01Al_2O_3$: $64H_2O$. Alkali-treated ZSM-5-300 was prepared with a solution of Na_2CO_3 and TPAOH (0.1 M TPAOH, 0.2 M Na_2CO_3) at 353 K for 2 h and washed with deionized water until neutral. The sample is designated as NaZ5-300-AT. Z5-300-AT was obtained by three repeated ion exchanges with 1.0 M NH_4NO_3 solution at 353 K for 1 h. The product was filtered and thoroughly washed with deionized water, dried at 373 K for 10 h, finally, Z5-300-AT ammonium form samples were obtained after calcination at 813 K for 4 h.

2.1.5. Synthesis of S-1.

S-1 was prepared using TEOS as a silicon source; Tetrapropylammonium hydroxide (TPAOH, 1.2 M) was used as template and base. The molar composition of the mixture was 1TEOS:0.27TPAOH:$67H_2O$. After stirring at 308 K for 6 h, the mixture was placed in a Teflon-lined stainless steel autoclave at 443 K for 3 days. The zeolite product was filtered and thoroughly washed with deionized water, dried at 373 K for 10 h. The template was removed by static air calcination at 813 K for 6 h. The sample is designated as S-1.

2.1.6. Preparation of tandem catalysts.

A tandem catalyst is usually prepared by "dust mixing". Two components, i.e. ZnO/ZrO_2 and zeolite (Z5, Z5-AT, S-1, Z5-x, Z5-x-AT) were mixed with a mortar and pestle for 10 minutes with a solid mass ratio of 1:2 (special co except for 'instructions). The powder mixture was pressed, ground and sieved to 20-40 mesh (i.e. 380-830 μm) and the resulting catalyst was designated as ZnO/ZrO_2-zeolite.

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