

Catalytic performance of cerium modified Silicalite-1 molecular sieves in the conversion of methanol to propene

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Abstract: A series of cerium modified Silicalite-1 molecular sieves were prepared by incipient wetness impregnation and used as the catalysts in the conversion of methanol to propene (MTP). The cerium modified Silicalite-1 catalysts were characterized by X-ray diffraction (XRD), N₂ sorption, pyridine adsorption Fourier transform infrared spectroscopy (Py-FTIR) and temperature-programmed desorption of NH₃ (NH₃-TPD); their catalytic performance in MTP was evaluated in a continuous flow fixed-bed micro-reactor at atmospheric pressure and 450°C, with a methanol weight hourly space velocity (WHSV) of 9.6 h⁻¹. The results showed that Silicalite-1 exhibits superior catalytic performance in MTP in terms of catalytic stability and selectivity to propene, in comparison with the HZSM-5 zeolite with a SiO₂/Al₂O₃ molar ratio of 200. The introduction of Ce can effectively adjust the acid properties and pore structure of Silicalite-1; modification with an appropriate concentration of Ce can reduce the amount of strong acid sites and then enhance the catalytic performance of Silicalite-1 in MTP. Over the cerium modified Silicalite-1 with a CeO₂ content of 5.0%, the selectivity to propene is increased from 31.9% to 38.2% and the catalytic lifetime is extended from 51 to 72 h, in comparison with those over the parent Silicalite-1.

Keywords: methanol; propene; Silicalite-1; cerium; acidity

With the increasing demand for propene in recent years, more and more attention has been paid to the conversion reaction of methanol to propene (MTP)^[1–3], which is dependent on the performance of the used catalysts. Currently, HZSM-5 zeolite is one of the preferred catalysts in MTP reaction, owing to its high propene yield and good resistance to carbon deposition. So far, the well-developed Lurgi MTP process takes place over the HZSM-5 catalyst in four adiabatic fixed-bed reactors, which gives a single selectivity of 42.0% to propene at a methanol conversion of about 90.0% for 8000 h^[4]. However, seeking for alternative ways to improve the selectivity to propene and catalytic stability is still the focus of current researches. It has been found that both the density and strength of acid sites decrease with the decrease of Al content in the HZSM-5 zeolite, which may effectively enhance the selectivity to propene and suppress the carbonaceous deposition^[5–8].

In recent years, Silicalite-1 zeolite has played an important role in the field of shape-selective catalysis. Perfect Silicalite-1 is

formed almost entirely by Si–O–Si bonds; it is lipophilic and hydrophobic. When subjected to thermal treatments, the partial loss of tetrahedral Si from the framework results in the simultaneous generation of extra-framework species and lattice defects, thus showing a high density of internal OH groups^[9]. The presence of these hydroxylated nanocavities makes this porous material less hydrophobic than the perfect one and show a very mild acidity. Heitmann et al^[10] pointed out that the silanol nests in Silicalite-1 were catalytically active for the Beckmann rearrangement reaction, with high product selectivity. Bonelli et al^[11] further suggested that the existence of terminal hydroxyl groups could accelerate the catalyst deactivation. Flego et al^[12] also reported that cyclohexanone oxime could react with the hydroxyl groups at 200°C. Besides, Thibault-Starzyk et al^[13] found that the deposited coke were mainly located on non-acidic silanol groups inside the micropores; the presence of silanol defects could significantly extend the catalyst lifetime. Likewise, it was also found that Silicalite-1 exhibited high selectivity to

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propene in the cracking reaction of butene, owing to its weak acidity^[14]. However, there are few reports on the application of Silicalite-1 in MTP reaction.

MTP reaction is a typical acid-catalyzed and shape-selective reaction process; the product selectivity and catalyst stability depend strongly on the acidity and diffusion properties of HZSM-5^[15]. Many efforts have been devoted to improving the catalytic performance of HZSM-5, such as metal/nonmetal modification^[16,17], high temperature steam treatment^[18], multi-level pore structure construction^[19,20], and so on. Therefore, on the basis of a comparison in the catalytic performance between Silicalite-1 and H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$) zeolites for MTP reaction, a series of Ce-modified Silicalite-1 catalysts were prepared in this work and characterized by XRD, N_2 sorption, Py-FTIR and NH_3 -TPD to investigate the effect of Ce addition on the catalytic performance of Silicalite-1 in MTP. The insight shown in this work should be of benefits to development of efficient MTP catalysts.

1 Experimental

1.1 Catalyst preparation

Silicalite-1 zeolite was prepared through the traditional hydrothermal crystallization method, with sodium silicate ($\text{Na}_2\text{SiO}_2 \cdot 9\text{H}_2\text{O}$, AR) as silica source, tetrabutylammonium bromide (TBABr, 99.0%) as template, and sulfuric acid (H_2SO_4 , 95.0%–98.0%) as pH value regulator. All of the reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. In the synthesis, a certain amount of TBABr was dissolved in the deionized water to reach a homogenous state, a corresponding amount of $\text{Na}_2\text{SiO}_2 \cdot 9\text{H}_2\text{O}$ was then added dropwise into the solution; an additional amount of deionized water was added. After stirring vigorously at room temperature for 2 h, the gel was transferred into a static Teflon-lined stainless-steel autoclave and crystallized at 180°C under autogeneous pressure for 8 h. The synthesized products were filtered, washed, and then dried at 140°C overnight, followed by calcination at 550°C for 3 h. After that, the NaZSM-5 material obtained was turned into H-form by three consecutive ion-exchange processes with 1 mol/L NH_4NO_3 solution at 80°C for 2 h, dried at 140°C and calcined again at 550°C for 2 h, which is then denoted as S-1. The HZSM-5 zeolite with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 200, denoted as HZ-5, was purchased from the Catalyst Plant of Nankai University.

The Ce-modified silicalite-1 catalysts were prepared by incipient wetness impregnation method. Silicalite-1 were immersed in the aqueous solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with an appropriate concentration at room temperature for 6–12 h, which was then dried at 120°C and calcined at 550°C for 2 h. The Ce-modified catalyst samples are denoted as $x\text{Ce}/\text{S}-1$, where x represents the mass percentage of CeO_2 in the

catalysts. Prior to the catalytic activity tests, all the catalysts were pressed, crushed and sieved into 40–60 mesh particles.

1.2 Catalyst characterization

The XRD patterns were recorded on an X'Pert PRO MPD diffractometer (PANalytical Co., Netherlands, $\lambda = 0.15406$ nm) at 40 kV and 40 mA, using Cu $K\alpha$ radiation with a scanning speed of 10(°)/min and scanning range from 5° to 75°. X-ray fluorescence spectroscopy (PANalytical Co., Netherlands, Axios) was used to analyze the composition of the samples at 60 kV and 160 mA.

The nitrogen adsorption-desorption isotherms were measured at 77 K on an ASAP 2010 apparatus (Micromeritics). Before the measurements, the samples were degassed at 300°C and 1.0×10^{-6} Pa for 4 h. The total surface area was calculated from the Brunauer-Emmett-Teller (BET) equation and the external surface area and the pore volume were determined by the t -plot method.

Pyridine adsorption Fourier-transform infrared spectroscopy (Py-FTIR) measurements were conducted on a Tensor 27 FTIR spectrometer (Bruker) with MCT-A detector, automatic gain of 64 and scanning range of 4000–600 cm^{-1} . Temperature-programmed desorption of ammonia (NH_3 -TPD) was conducted on a TP-5079 apparatus (Xianquan, Tianjin, Co.). In a typical measurement, about 100 mg sample was initially pretreated with flowing helium at 600°C for 0.5 h, cooled down to 100°C and saturated with NH_3 ; the sample was then purged with He until a stable TPD signal was attained. Finally, the temperature of the sample was increased from 100 to 550°C at a heating rate of 10°C/min. The amount of NH_3 desorbed in millimole at the corresponding temperature was measured with an on-line thermal conductivity detector (TCD).

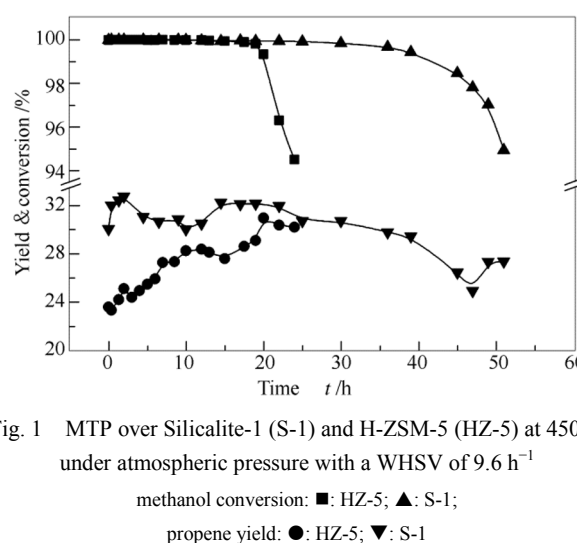


Fig. 1 MTP over Silicalite-1 (S-1) and H-ZSM-5 (HZ-5) at 450°C under atmospheric pressure with a WHSV of 9.6 h^{-1}

methanol conversion: ■: HZ-5; ▲: S-1;
propene yield: ●: HZ-5; ▼: S-1

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