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New route for light olefins production from chloromethane over HSAPO-34 molecular sieve

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Abstract

HSAPO-34 molecular sieve was employed in chloromethane conversion and showed high performance in activity and selectivity in production of light olefins. Our detailed IR investigation allowed the identification of the active sites and the adsorbed species and demonstrated that the conversion started from 350 °C with alkoxy group as the intermediate. The fixed-bed catalytic testing evidenced that in the range of 350–500 °C, 70–80% of chloromethane was transferred to ethylene, propylene and butenes. Increasing reaction temperature favors the conversion and enhances the yield of lighter olefins. A very important reversible phenomenon, the breaking of Al–O–P bonds upon adsorption of HCl, a main product of reaction to generate a large amount of P–OH groups and the recovery of Al–O–P upon removal of HCl was revealed.

Keywords: Chloromethane; Light olefins; Hydrocarbons; HSAPO-34; FTIR; Catalytic tests; Reaction mechanism

1. Introduction

Facing the sharp and ceaseless increase in price of crude oil, the development of efficient routes for higher hydrocarbons production through methane transformation becomes one important and urgent issue. Some promising results appeared to be of great importance in the field of catalytic conversion of chloromethane to higher hydrocarbons. In 1985, Olah et al. described a very interesting three-steps catalysis process for the transformation of methane to higher hydrocarbons through monohalogenation of methane, hydrolysis of halide methane to methanol, and then the MTG reaction on HZSM-5 [1]. In 1988, Taylor et al. invented a cyclic process for the production of gasoline from methane with chloromethane as the intermediate [2,3] and the transformation was reduced to two stages, i.e. the oxyhydrochlorination (OHC) for production of CH_3Cl from methane, and MTG for directly transferring methyl chloride to gasoline, with HCl as the by-product, which can be recycled for the first step. This is a quite innovative process, applicable in industry. The corrosion problem of the produced HCl can be resolved. For the chloromethane transformation, compared with other large pore zeolite catalysts, both cationic and protonic ZSM-5 appeared to be the most promising catalyst due to their high activity and long life in the reaction and a strong reduction in the coke formation [4–9]. All above studies indicated that, just as the well known MTO or MTG process, chloromethane transformation to higher hydrocarbons could be a potential and an efficient alternative route for methane utilization.

Compared with a large series of studies carried out with classical zeolites, the SAPO type molecular sieve catalyst seemed to be neglected while SAPO-34 with excellent performance in MTO process [10–12] could be a very promising catalyst for chloromethane conversion to other hydrocarbons, especially to light olefins, such as ethylene and propylene due to its small channel size. In regards with

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chemical composition difference between classical zeolites and SAPO molecular sieves, the nature of the active sites, the activation and transformation of chloromethane on SAPO-34 should be quite different and merit a detailed investigation. In this study, for the first time, SAPO-34 was employed as the catalyst for chloromethane conversion, which was carried out in a fixed-bed reactor and was also followed by in situ FTIR spectroscopy.

2. Experimental

2.1. Synthesis of SAPO-34

SAPO-34 was synthesized by the hydrothermal method [13,14] from a gel composition of $3.0R:1.0P_2O_5:1.0Al_2O_3:0.8SiO_2:50H_2O$, where R is triethylamine as the template. Pseudoboehmite, orthophosphoric acid (85 wt.%) and colloidal silica were used as the sources of aluminum, phosphorus and silicon, respectively. The chemical composition of synthesized SAPO-34 after removal of organic template is $Al_{0.49}P_{0.41}Si_{0.10}O_2$. Two samples with the same gel composition but with different synthesis scales (100 ml and large scale combining an improve technique) were prepared while both give the same chemical composition, indicating the good reproducibility of our synthesis. The FTIR study and the effect of reaction temperature by catalytic testing used the sample synthesized with 100 ml autoclave and the effect of reaction time employed the second sample.

2.2. In situ FTIR study

Self-supported SAPO-34 wafers (17 mg/cm^2) were first calcined in a flow of dry oxygen at 450 °C for 10 h and then in vacuum for 4 h. After cooling to room temperature, the spectra of SAPO-34 phase and gas phase were recorded as reference using a Fourier Transform Spectrometer (Perkin-Elmer Spectrum 2000). The adsorption of known amounts of CH_3Cl (Aldrich, 99.5%) was then conducted on the wafers. The conversion of CH_3Cl was performed in situ from 250 to 500 °C for 15 min with a CH_3Cl molecule loading of 45 molecules per unit cell (m/u.c.). After reaction, the samples were cooled in liquid nitrogen to stop the reaction and the IR spectra of both gas phase in the IR cell and adsorbed phase with the catalyst were recorded.

2.3. Reaction testing

The catalytic tests were performed using a fixed-bed reactor at atmosphere pressure. 0.62 g of catalyst was loaded into a quartz reactor with an inner diameter of 5 mm. The sample was pretreated in a flow of dry nitrogen at 500 °C for 1 h and then the atmosphere was replaced by nitrogen and chloromethane (the molar ratio of N_2/CH_3Cl was 1) and the temperature of reactor was adjusted to the desired temperature. The temperature range studied was 350–500 °C. The weight hourly space velocity (WHSV) was 3.17 h^{-1} for chloromethane. The reaction products were analyzed on-line by a Varian GC3800 gas chromatograph equipped with a FID detector and a PONA capillary column.

3. Results and discussion

3.1. FTIR study on the surface hydroxyls of SAPO-34 and adsorption and conversion of chloromethane

Fig. 1 gives the spectra of activated SAPO-34 and adsorbed species upon adsorption of CH_3Cl with different loadings (Fig. 1A) and those upon conversion of CH_3Cl on SAPO-34 at different temperatures with a CH_3Cl loading of 45 m/u.c. (Fig. 1B), the gas phase being subtracted. SAPO-34 after activation (Fig. 1A(a)) gives four peaks in the range of 3000–4000 cm^{-1} representing four types of hydroxyl groups. Two peaks at 3625 and 3598 cm^{-1} can be attributed to two types of Si(OH)Al groups differed in their localization. The bridged group with $\upsilon = 3598$ cm^{-1} is assumed to be localized in the hexagonal prism, forming an H–bond with adjacent oxygen atoms of the framework while the isolated bridged OH groups pointing towards the center of the elliptical cages give the vibration frequency at 3625 cm^{-1} [15–18]. These two types of OH groups have been considered to have similar acidic properties and to be the active sites for acid-catalyzing reaction [19,20]. The other two peaks at 3675 and 3743 cm^{-1}, with very low intensity are assigned to P–OH and Si–OH, respectively, which are generated by the defect sites of the surface of the crystal sample.

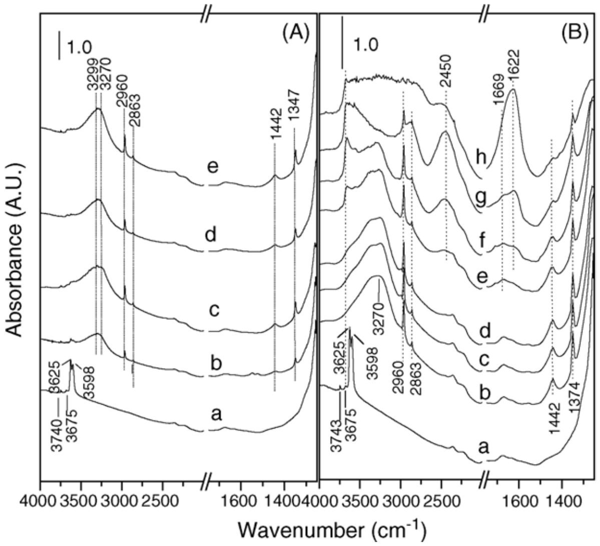

Fig. 1. FTIR spectra of activated SAPO-34 (a) and adsorbed species upon adsorption of CH_3Cl with different loadings (1A) (m/u.c.) of 15 (b); 30 (c); 45 (d), and 60 (e) and conversion of CH_3Cl on SAPO-34 with a CH_3Cl loading of 45 m/u.c. (1B) At reaction temperature (°C): (a) activated SAPO-34; (b) RT; (c) 250; (d) 300; (e) 350; (f) 400; (g) 450 and (h) 500 for 15 min.