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.

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 CH3Cl 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...
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:1.0P2O5:1.0Al2O3:0.8SiO2:50H2O, 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 Al0.49P0.41Si0.10O2. 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/cm2) 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 CH3Cl (Aldrich, 99.5%) was then conducted on the wafers. The conversion of CH3Cl was performed in situ from 250 to 500 °C for 15 min with a CH3Cl molecule loading of 45 m/u.c. (m/u.c.) of 15 (b); 30 (c); 45 (d), and 60 (e) and conversion of CH3Cl on SAPO-34 with a CH3Cl 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.

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 CH3Cl with different loadings (Fig. 1A) and those upon conversion of CH3Cl on SAPO-34 at different temperatures with a CH3Cl 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, 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.
Upon addition of 15, 30, 45 and 60 m.u.c. of CH$_3$Cl at room temperature into the IR reactor, the bridged hydroxyl bands at 3625 and 3598 cm$^{-1}$ decrease in intensity and disappear completely at a loading of 30 m.u.c., indicating that SAPO-34 molecular sieve has an adsorption capacity of around 30 m.u.c. for CH$_3$Cl. Simultaneously, four new and sharp bands appear at 2960, 2863, 1442 and 1347 cm$^{-1}$, attributed to the anti-symmetric or symmetric stretching and bending vibrations of methyl group of CH$_3$Cl, respectively, indicating the adsorption of CH$_3$Cl molecules on the catalyst. The very broad and intense band which can be decomposed by a Winspec program to two overlapped components centered at 3299 and 3270 cm$^{-1}$, respectively, is also observed and can be attributed to the interaction of CH$_3$Cl with the two bridged hydroxyl groups (Fig. 1B(c and d)) show even clearer the existence of two components. The interaction with CH$_3$Cl shifts the two hydroxyls at 3625 and 3598 cm$^{-1}$ to lower wave numbers. This observation suggests that both bridging Si(OH)Al groups are accessible to CH$_3$Cl molecules and could be the active sites in the CH$_3$Cl conversion. When reaction was performed at 250 and 300 °C for 15 min (Fig. 1B(c and d)), no significant change in IR spectrum can be noted, which means that no conversion occurs at temperature <300 °C. Some interesting and relevant changes appear from 350 °C onwards (Fig. 1B(e)), indicating that the conversion may start from this temperature. From 350 to 450 °C, the intensity of the four peaks at 2960, 2863, 1442 and 1347 cm$^{-1}$ due to the methyl group of CH$_3$Cl decreases, suggesting that the transformation occurs. At the same time, with the consumption of CH$_3$Cl molecules, the bands at 3299 and 3270 cm$^{-1}$, due to the CH$_3$Cl interaction with the active sites, also lose their intensity. A band at around 1669 cm$^{-1}$ appears from 350 °C and becomes more important with increasing temperature. This band can be attributed to the stretching vibration of C=C, indicating the generation of alkenes from CH$_3$Cl conversion over the surface of the catalyst.

It is worthy to note the appearance of a series of broad bands at around 2878, 2450 and 1622 cm$^{-1}$ (the band of 2878 cm$^{-1}$ is overlapped with the bands of 2960 and 2863 cm$^{-1}$) and their intensity increases with increasing reaction temperature. These three broad bands may come from the H–bonding complex and be attributed to the perturbed OH vibration, because they are quite similar to the triplet A, B, C bands of hydroxyl group as previously reported [21,22]. Usually, for the H–bonding complex, the A–B–C pattern with broad and intense absorbance at around 2800, 2400 and 1700 cm$^{-1}$, is caused by a Femi resonance between out-of-plane deformation vibration of bridged OH group and the perturbed hydrogen bound OH group due to O–H…X–H formation.

The observation of triplet A–B–C pattern as soon as the conversion occurs signifies that HCl is immediately generated from the dehalogenation of CH$_3$Cl with the occurrence of the reaction. Strong H–bond complex (A–B–C pattern at 2878, 2450 and 1622 cm$^{-1}$) is due to the strong interaction between Si(OH)Al and HCl. Another quite interesting fact is that the intensity of absorption at 3675 cm$^{-1}$ increases significantly as soon as the occurrence of the reaction at 350 °C (Fig. 1B(e)). For the activated sample, this peak is assigned to the P–OH of SAPO-34. Its increase in intensity indicates the generation of a large amount of P–OH during the chloromethane conversion, which may result from HCl adsorption on aluminophosphate framework. The dissociative HCl adsorption on the framework may break the bond of Al–O–P and give the new bonding of P–OH and AlCl. Similar dissociative HCl adsorption was previously reported in the study of HCl adsorption on Al$_2$O$_3$ surface [23]. All the above observations (A–B–C triplet pattern and the increase of P–OH groups in intensity) reveal that the elimination of HCl from CH$_3$Cl, generating simultaneously the methoxy groups on catalyst is the first step of chloromethane conversion and the precursor of the C–C bond formation. This is in complete agreement with previous reports [6,9].

Further increasing the temperature to 500 °C, in the hydroxyl absorption zone (3700–3000 cm$^{-1}$), a larger band appears. This can be explained by the interaction of the bridged hydroxyls with the different alkenes. The absorbance of hydroxyls becomes very complicated for this reason.

### 3.2. Reaction testing

#### 3.2.1. Effect of reaction temperature

The data were recorded after 65 min reaction. The conversion evolution as a function of temperature depicted in Fig. 2 shows that increasing the temperature favors the conversion. A conversion of 70% is reached at 500 °C. Fig. 3 gives the product distribution in carbon number. It is quite interesting to observe that C$_2$–C$_4$ hydrocarbons are the main products of this reaction. This is significantly different from the products obtained on a series of large pore zeolite catalysts, such as X, Y, EMT, Beta and MOR [5,6,9] and

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Fig. 2. Chloromethane conversion at different temperatures.
should be attributed to the 8-ring pore structure of SAPO-34. The narrow pore opening favors the production of light hydrocarbons and prohibits the formation of larger hydrocarbon molecules. The higher temperature favors the generation of smaller products. In fact, at relatively low reaction temperature, the formation of C\textsubscript{3} products (propylene and propane) predominates. At 450 °C, the selectivity of C\textsubscript{2} and C\textsubscript{3} attain to the same level, while the C\textsubscript{2} products become the most abundant at 500 °C. The production of methane increases slightly with increasing temperature, which may result from the cracking of the hydrocarbon products.

The distribution of the products as a function of reaction temperature is detailed in Fig. 4. Light alkenes such as ethylene, propylene and butenes in the studied temperature range are the main products of the reaction (with a small amount of aromatics). At any reaction temperature, practically around 80% products are attributed to ethylene, propylene and butenes, indicating that SAPO-34 is a very selective catalyst for the production of light alkenes. With increasing reaction temperature, the selectivity of ethylene increases and that of propylene and butenes decreases. The highest ethylene selectivity (40%) in the studied temperature range can be obtained at 500 °C. Only a small amount of light alkanes can be observed at 350–450 °C. The products heavier than C\textsubscript{5} account for 15–20% of all the products in this temperature range, which may come from oligomerization of light alkenes or the alkylation of light alkanes with alkenes. At 500 °C, methane becomes more prominent than other light alkanes, which may result from cracking favored thermodynamically by the high temperature. This was previously observed with other zeolite catalysts [5,6,9]. In the complete temperature range, only traces of aromatic products were observed. During the reaction, HCl is also observed in the products (not listed in the product distribution).

ZSM-5 has been proved to be the most successful catalyst in chloromethane transformation compared with Y, Beta, MOR and EMT zeolites [4,7]. For ZSM-5, usually the products in C\textsubscript{3}–C\textsubscript{6} boiling range are the main products, similar to the product distribution of ZSM-5 catalyzed MTG process. The group composition of products depends on the modification of the catalysts. In Taylor’s work, chloromethane was mainly transferred to aromatics and paraffins [3]. In a very recent publication, ethylene and propane appeared as the main products with cationic exchanged ZSM-5 [5,6]. P or Mg modified ZSM-5 catalysts were used in Sun’s study and the transformation gave an alternative products distribution with remarkable propylene and butenes generation [7]. Here SAPO-34, with 8-ring pore opening and medium acidity demonstrates its interesting behavior, such as high selectivity for light olefins.
production, similar to its excellent performance in MTO process [11,12].

3.2.2. Effect of run length

This was performed at 450 °C. Fig. 5 gives the variation of conversion as a function of run length. No change can be noted for the first hour of reaction while the conversion drops from 87 to 70% after 2 h reaction. SAPO-34 is not as stable as expected and exhibits a relatively fast deactivation. The product distribution as a function of reaction time is analyzed and shown in Fig. 6. It can be seen that the selectivity for C\textsubscript{3}H\textsubscript{6} and C\textsubscript{4}H\textsubscript{8} remains unchanged while that for C\textsubscript{2}H\textsubscript{4} increases sharply. We observe also a significant drop in selectivity for C\textsubscript{3} alkane and C\textsubscript{5+}, particularly at the initial reaction stage. No production of BTX is noted. The high selectivity for C\textsubscript{3} and C\textsubscript{5+} formation at initial reaction stage indicates quick formation of the C–C bonds and especially the rapid growth of C–C chain length. Due to the very special cage form and small opening of SAPO-34 molecular sieve, the molecules formed in the cage can continue to grow and cannot easily escape from the cage. Some coke formation is still possible, modifying the activity and particularly the selectivity. That is why we have no BTX formation in the products but we still have a deactivation of catalyst. The deeply polymerized species deposited on the active sites revealed by our previous IR study confirms the above hypothesis. This was already observed in the MTO process from methanol. Usually, it is thought that SAPO-34 with small pore is very sensitive for the coke formation. Coke formation modifies the pore opening, which is very effective to the olefin products production. Another possibility for the unexpected deactivation is probably the formation of large amount of P–OH groups and Al–Cl bonds in the framework, which can affect the acidity of Si–OH–Al groups, in consequence the activity of catalyst. However, some more work is necessary if some conclusions of this kind can be drawn.

Moreover, the coke formation is an interesting topic for MTO process from methanol and it was found that in the MTO process, the better catalyst is not fresh SAPO-34, but with some coke. A fluidized-bed process with continuous coke removal could be considered.

4. Conclusion

SAPO-34 molecular sieve is a very active and selective catalyst for the production of light alkenes from CH\textsubscript{3}Cl transformation although the stability still needs to be improved. The conversion and product distribution varied with temperature. Increasing the temperature favored the chloromethane conversion and the yield of light hydrocarbons. In the temperature range of 350–500 °C, 70–80% selectivity of light alkenes can be obtained. The dehalogenation of CH\textsubscript{3}Cl was the first step of reaction conducting to immediate C–C formation. Alkenes and HCl appeared as the main products, which stay on the catalyst surface. The dissociative adsorption of HCl on Al–O–P generated new P–OH while the removal of HCl can restore the Al–O–P bonds. This is a reversible process and observed for the first time with SAPO-34 under reaction process.

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Reference