Mechanistic elucidation of chloromethane transformation over SAPO-34 using deuterated probe molecule: A FTIR study on the surface evolution of catalyst

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Abstract

Adsorption and transformation of chloromethane over SAPO-34 catalyst were studied using deuterated CD_3Cl as probe by in situ FTIR spectroscopy and compared with CH_3Cl. The detection of the deuterated hydroxyls Si(OD)Al indicated the existence of the H and D exchange reaction due to the interaction of Si(OH)Al and DCl molecules produced by CD_3Cl conversion. The reversible breaking of Al–O–P bonds as a result of the interaction of Al–O–P with the produced DCl molecules has been clearly evidenced by the observation of P–OD and P–OD–Al species. Increasing CD_3Cl loading favors C=C generation and higher hydrocarbons formation. A possible surface species evolution and formation during CD_3Cl transformation over SAPO-34 catalyst is proposed.
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1. Introduction

Chloromethane transformation to higher hydrocarbons, as one of the potential routes for natural gas utilization has attracted many interests from industry and academy in the past 20 years and gets new important attention due to the recent sharp and constant increase in crude oil price [1–10]. The first work from Olah et al. described a very interesting and attractive three-step catalysis process for the transformation of methane to higher hydrocarbon through halide methane [1]. In 1988, Taylor et al. gave a more practical cycle process for the production of gasoline from methane with chloromethane as the intermediate. The transformation was thus reduced to two stages with the first stage of chloromethane production and the second for transferring methyl chloride directly to gasoline [2]. Among the catalysts for chloromethane transformation published in the lit-

erature, ZSM-5 zeolite has been proved to be the most successful because of its high activity and long life in the reaction [3–5]. In our very recent study, SAPO-34 has exhibited very high selectivity and strong potential for light olefins production from chloromethane transformation [6,7].

There are undoubtedly many parallels between MTO and MTG processes starting from methanol and CH_3Cl to higher hydrocarbons. With the same purpose of natural gas utilization, both of them transform methane in an indirect way with methane derivatives as intermediates. While the important distinction between chloromethane and methanol transformation is that the proposed intermediates derived from CH_3OH, such as CH_3OCH_3, are not accessible in CH_3Cl conversion. No dehydration occurs in chlromethane transformation, while HCl instead of H_2O will be generated and be involved in the surface adsorption and conversion. We have observed very special interaction between the generated HCl and hydrocarbons and the surface active sites of SAPO-34 [6–8]. It is very closely related to the mechanistic consequence of chloromethane conversion over the SAPO molecular sieve surface.

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For a better elucidation of reaction mechanism and in order to improve further the performance of SAPO-34 to develop more efficient and industrialisable catalysts for chloromethane conversion to light olefins or gasoline, CD_3Cl was used in the present study to identify surface species and to follow the evolution of catalyst surface during adsorption and transformation of deuterated chloromethane.

2. Experimental

The synthesis and structural characteristics of SAPO-34 have been reported else where [6,8]. The chemical composition of synthesized SAPO-34 after removal of organic template is $Al_{0.49}P_{0.41}Si_{0.10}O_2$. For in situ FTIR study, self-supported SAPO-34 wafers (15 mg/cm^2) were placed in a quartz cell and 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 spectrum of activated SAPO-34 was recorded using a Fourier Transform Spectrometer (Perkin–Elmer Spectrum 2000). The adsorption of known amounts of CH_3Cl or CD_3Cl (5, 15 and 30 molecules per unit cell (m/uc)) was then conducted on the wafers. The chloromethane and deuterated chloromethane were purchased from Aldrich Chemical Company (99.5%). The conversion was carried out at 450 °C for 15 min. After reaction, the samples were immediately cooled in liquid nitrogen to stop the reaction and the IR spectra of the catalyst with adsorbed phase were recorded.

3. Results and discussion

3.1. Surface hydroxyls of SAPO-34 and adsorption of CH_3Cl and CD_3Cl

Fig. 1 gives the spectra of the activated SAPO-34 and the adsorption of CH_3Cl and CD_3Cl with different loadings. Four peaks in the range of 3000–4000 cm^{-1} have been revealed in the spectrum of activated SAPO-34 and represent four types of hydroxyl groups [11,12]. The peaks with very low intensity at 3675 and 3740 cm^{-1} are attributed to terminal P–OH and Si–OH, respectively, as a result of the surface defects of SAPO-34. Two other peaks with high intensity at 3625 and 3598 cm^{-1} are from the absorbance of bridged hydroxyl of Si(OH)Al. The bridged group with $v = 3598$ 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}. These two kinds of bridged hydroxyl groups are considered to be the active sites of SAPO-34 catalyst [13,14].

Adsorption of 5 m/uc of CH_3Cl at room temperature gives rise to the intensity decrease of bridged hydroxyl bands at 3625 and 3598 cm^{-1} and the immediate appearance of a new and broad band centered at 3270 cm^{-1} (Fig. 1b), which can be attributed to the interaction of
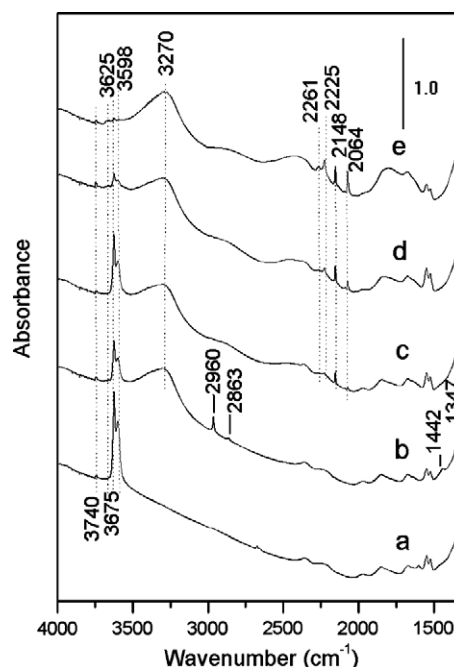

Fig. 1. (a) FTIR spectra of adsorption of CH_3Cl and CD_3Cl on activated SAPO-34, (b) activated SAPO-34, (c) adsorption of CH_3Cl with a loading of 5 m/uc, and adsorption of CD_3Cl with a loading of 5 m/uc (d), 15 m/uc (e) and 30 m/uc.

CH_3Cl with two bridged hydroxyl groups [9,15]. For CD_3Cl adsorption (Fig. 1c–e), in the hydroxyl range, the broad band appears at the same wave number, 3270 cm^{-1}, and its intensity increases with CD_3Cl loading, being similar to the observation upon adsorption of increasing amount of CH_3Cl [6]. This observation suggests that the interaction between bridged hydroxyls of SAPO-34 with chloromethane is not affected by the replacement of protons by deuterium in chloromethane and that this interaction occurs indeed through the interaction of protons of framework hydroxyls with negatively charged chlorine atoms as we previously proposed [5–10]. It is noticed that simultaneously with the observation of the new broad band at 3270 cm^{-1}, four new and sharp bands at 2960, 2863, 1442 and 1347 cm^{-1} appear in CH_3Cl adsorption spectra and are attributed to the anti-symmetric or symmetric stretching and bending vibrations of methyl group of CH_3Cl, respectively, indicating the adsorption of chloromethane molecules on the catalyst. CD_3Cl addition into IR reactor generates also four new bands, but at 2261, 2225, 2148 and 2064 cm^{-1}, which can be assigned to the anti-symmetric or symmetric stretching vibration of C–D bond in deuterated methyl of CD_3. With more CD_3Cl molecule loading, these new bands at 3270, 2261, 2225, 2148 and 2064 cm^{-1} are intensified. Si(OH)Al absorbance further loses their intensity and almost disappear at the CD_3Cl loading of 30 m/uc (Fig. 1e). These observations indicated that two kinds of bridged hydroxyls present in SAPO-34 could be the active sites in the CD_3Cl conversion due to their accessibility to and their interaction with CD_3Cl

molecules. because of the complete disappearance of these two hydroxyl groups, all the hydroxyl sites are occupied and saturated by the (deuterated) chloromethane molecules. This indicates also that all the bridged hydroxyl groups are accessible to the chloromethane molecules.

3.2. Transformation of CH_3Cl and CD_3Cl over SAPO-34

The FTIR spectra of adsorption and conversion of CH_3Cl and CD_3Cl over SAPO-34 with a chloromethane loading of 15 m/uc were depicted in Fig. 2a and b, respectively. After 15 min of reaction at 450 °C, the bands from the interaction of Si(OH)Al with CH_3Cl or CD_3Cl (3270 cm^{-1}) and the bands stemming from methyl group (2960, 2863, 1442 and 1347 cm^{-1} from CH_3Cl and 2261, 2225, 2148 and 2064 cm^{-1} from CD_3Cl) decrease significantly in intensity, indicating the conversion of chloromethane. The simultaneous appearance of the broad band at 3000–3500 cm^{-1}, due to interaction of Si(OH)Al and alkene products, and the band at 1609 cm^{-1} from the adsorbed C=C species in Fig. 2a–c, proves the new C–C bond formation during the reaction [6]. While for CD_3Cl transformation, a similar broad absorbance is observed at 2000–2700 cm^{-1} with the consumption of the broad band at 3270 cm^{-1} (Fig. 2b and c). Two bands at 1590 and 1381 cm^{-1} are also revealed. This indicates that alkene species with C=C bond are also generated during CD_3Cl transformation as CH_3Cl. The wide absorbance in 2000–2700 cm^{-1} may therefore stem from the deuterated hydroxyls interacting with formed alkene products, just as the condition of CH_3Cl transformation.

After reaction, the system is evacuated to remove the products present in gas phase and adsorbed phase. With

evacuation at room temperature for 30 min (Fig. 2b–d), compared to the spectrum of CH_3Cl transformation in Fig. 2a–d, some new peaks, such as 2730, 2665, 2651, 2607, 888 and 862 cm^{-1}, appear in the CD_3Cl conversion spectra. Among them, 2665 and 2651 cm^{-1} should be attributed to H–D exchanged bridged hydroxyl Si(OD)Al [16]. The bending vibration mode of Si(OH)Al usually falls in 1000–1300 cm^{-1} region of lattice vibration, while the bending mode Si(OD)Al is visible with the absorbance at 888 and 862 cm^{-1} [17,18]. This suggests a very important phenomenon that after reaction, some bridged hydroxyls Si(OD)Al are generated, i. e. part of deuterium atoms of CD_3Cl was transferred to hydroxyl groups of SAPO-34.

3.3. Interaction between surface hydroxyls and adsorbed species

HCl and olefins have been proved by FTIR and catalytic testing as main products in chloromethane transformation using SAPO-34 as catalyst [6]. When deuterated chloromethane CD_3Cl is used as feed, logically DCl and $(CD=CD)_n$ will be generated during the transformation and followed adsorption of DCl and $(CD=CD)_n$ may also occur on SAPO-34 surface.

In our previous work, the FTIR results show some special adsorbed species, providing useful information for elucidating the interaction between the active sites of catalyst with reactant and products. Three shifts of Si(OH)Al caused by three adsorption species have been observed during the adsorption and conversion of chloromethane. The interaction between CH_3Cl and Si(OH)Al with the absorbance shift of bridged hydroxyl bands at 3625 and 3598–3270 cm^{-1} is related to the chloromethane adsorption.

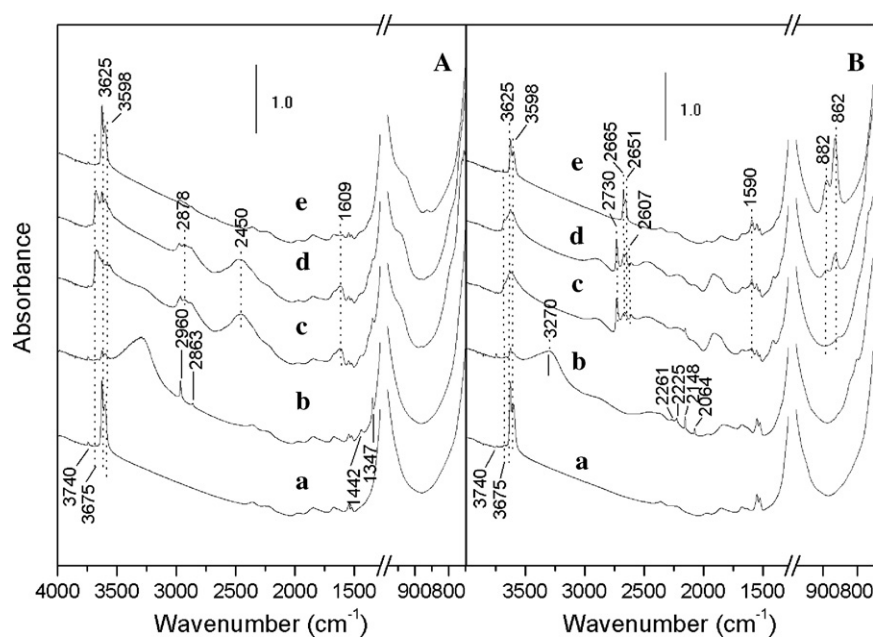Fig. 2. FTIR spectra of chloromethane adsorption (15 m/uc) and conversion, A: CH_3Cl, B: CD_3Cl, (a) activated SAPO-34, (b) adsorption at RT, (c) reaction at 450 °C for 15 min, (d) evacuation at RT for 30 min, (e) evacuation at 150 °C for 60 min.

The same interaction and corresponding Si(OH)Al absorbance shift could be observed in the present work when CH_3Cl is replaced by CD_3Cl. During CD_3Cl transformation over SAPO-34 surface, bridged deuterated hydroxyls, Si(OD)Al with absorbance at 2665 and 2651 cm^{-1}, are generated with H–D exchange [16]. The interaction of alkene products with Si(OH)Al and Si(OD)Al presents at the same time with broad absorbance at 3000–3700 cm^{-1} and 2000–2700 cm^{-1} (Fig. 2b and c), respectively. While for CH_3Cl transformation given in Fig. 2a–c, we can only see the Si(OH)Al shift to a broad range of 3000–3700 cm^{-1}, due to the adsorption of alkenes on bridged hydroxyls. HCl adsorption on Si(OH)Al brings about three broad bands at 2878, 2450 and 1609 cm^{-1} from H-bonding complex [6]. DCl adsorption in the present study is thus strongly complicated by the coexistence of Si(OH)Al and Si(OD)Al groups.

The appearance of other two new peaks at 2730 and 2607 cm^{-1} in OD group absorbance range during CD_3Cl transformation should be related to the other very important interaction. Previous work has shown that the dissociative HCl adsorption on the framework can induce the breaking of Al–O–P bonds and gives rise to a large number of P–OH. The absorbance at 2730 and 2607 cm^{-1} corresponds to the generation of P–OD and Al–OD–P during the reaction. Using CD_3Cl as reaction feed could thus generate deuterated surface species, such as P–OD and Al–OD–P.

Further evacuating the system at 150 °C for 1 h, most of adsorbed products could be removed and the absorbance of Si(OH)Al and Si(OD)Al restore their intensity (Fig. 1a–e and b–e). With the removal of DCl, the bands of P–OD and Al–OD–P at 2730 and 2607 cm^{-1} disappear, giving the proof for the reversible interaction of Al–O–P and adsorbed H(D)Cl. On the basis of the above observations and analysis, a possible surface species evolution during CD_3Cl transformation is proposed (Scheme 1).

3.4. The effect of CD_3Cl loading

The absorbances at 1550–1630 cm^{-1} appear in the spectra of CH_3Cl and CD_3Cl transformation, representing the C–C bond formation. Even after evacuation at 150 °C for 1 h, the absorbance is still observable indicating the coke deposition. To compare the species on catalyst surface after reaction, the spectrum of activated catalyst has been subtracted from the each spectrum at defined loading recorded after reaction and evacuation (Fig. 3).

The appearance of negative bands at 3598 and 3625 cm^{-1} in OH absorbance range and positive absorbance at 2665 and 2651 cm^{-1} in OD range prove the coexistence of bridged hydroxyl Si(OH)Al and Si(OD)Al species on SAPO-34 surface after CD_3Cl transformation. The intensity of negative and positive absorbance of Si(OH)Al and Si(OD)Al groups increases with CD_3Cl loading, indicating that more bridged hydroxyls appear in deuterated form upon CD_3Cl loading. The intensity
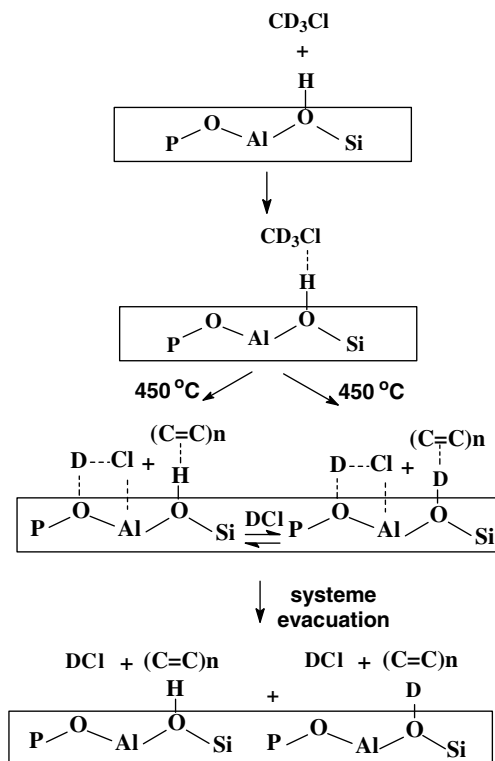
Scheme 1. Formation mechanism of possible surface species during CD_3Cl transformation over SAPO-34 catalyst.
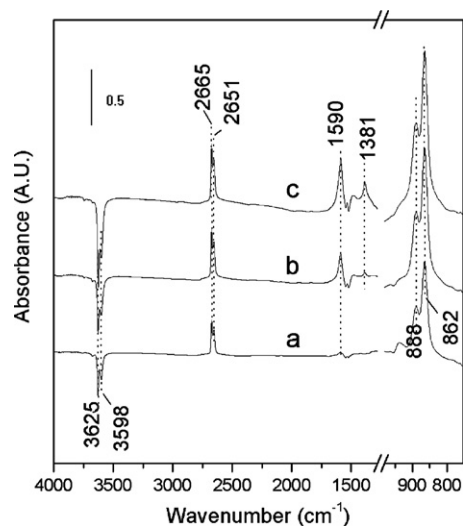

Fig. 3. FTIR spectra of the only adsorbed phase on catalyst after reaction with different CD_3Cl loadings (the spectrum of activated SAPO-34 is subtracted), (a) 5 m/uc, (b) 15 m/uc, (c) 30 m/uc.

increase of Si(OD)Al at 888 and 862 cm^{-1} also prove that more Si(OD)Al formation after CD_3Cl conversion with higher CD_3Cl loading.

The absorbance of 1590 cm^{-1} is present in all the three spectra and its intensity also varied with chloromethane loading. For 5 m/uc of CD_3Cl loading, just one very weak band appears. The spectrum obtained with 15 m/uc chloromethane loading shows a very clear absorbance at

1590 cm^{-1}. CD$_3$Cl (30 m/uc) loading gives rise to a more pronounced band at the same frequency. This absorbance is attributed to polymerized (C=C)$_n$ or more H-unsaturated cyclo-organic species, such as aromatic products. The peak at 1381 cm^{-1} appears simultaneously with that at 1590 cm^{-1}. However, its assignment is not clear yet.

Alkenes are the main products of chloromethane transformation over SAPO-34. After reaction, some products could not be removed from the catalyst surface. These products remaining adsorbed on the surface even after evacuation should be attributed to the products, which is too heavy to diffuse out of the 8-ring window of SAPO-34, or some more unsaturated products, such as coke precursor or even the deposited coke. The cyclic organic species are regarded as the reaction center, as described in the mechanism of hydrocarbon pool proposed by Kolbod and Haw [19,20]. The predominant conversion of high CD$_3$Cl loading chloromethane may stem from the formation of the large amount of cyclic organic species, which behaves as the scaffold for the assembly of light olefins, in agreement with our previous experimental study [6].

4. Conclusion

The FTIR investigation of deuterated chloromethane conversion gives a better elucidation on the catalytic transformation mechanism of chloromethane over SAPO-34. Our present results confirmed that at room temperature, there is no dissociation of CD$_3$Cl and there is no H–D exchange between CD$_3$Cl and Si(OH)Al. CD$_3$Cl reaction over catalyst surface gives rise to the deuteration of surface hydroxyls, which indicates again that the removal of DCl from CD$_3$Cl is the first step of the reaction and DCl produced can interact with the surface of the catalyst. The observation of POD and P(OD)Al further proves the dissociative adsorption of H(D)Cl on Al–O–P bond and this bond could be restored after evacuation at 150 °C. CD$_3$Cl loading has the effect on products generation. Polymerized alkenes or aromatic products are favored by the high CD$_3$Cl loading.

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