Catalysis Letters Vol. 109, Nos. 1–2, June 2006 (© 2006)
DOI: 10.1007/s10562-006-0063-5

Chloromethane conversion to higher hydrocarbons over zeolites and SAPOs

Dazhi Zhang,[a,c] Yingxu wei,[a] Lei Xu,[a] Aiping Du,[a,c] Fuxiang Chang,[a,c] Bao-lian Su,[b] and Zhongmin Liu[a,]*

[a]*Natural Gas Utilization and Applied Catalysis Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,*
457 Zhongshan Road, P.O. Box 110, Dalian 116023, P.R. China
[b]*Laboratoire de Chimie des Matériaux Inorganiques (CMI), The University of Namur (FUNDP), B-5000 Namur, Belgium*
[c]*Graduate school of the Chinese Academy of Sciences, Beijing 100039, P.R. China*

Received 4 January 2006; accepted 26 January 2006

Chloromethane transformations were carried out over zeolites and SAPOs and the conversion and product distribution differed from the porous structure and acidity of the catalysts. Chloromethane was mainly transferred to higher hydrocarbons in gasoline range over most of zeolite catalysts, while SAPOs molecular sieves, SAPO-34 and SAPO-5, showed high selectivity for light olefins production, such as ethylene, propylene and butenes. TG analysis was used to study the coke formation during the transformation and the acid difference of the catalysts was evidenced by Temperature programmed desorption of ammonia. HZSM-5, with high activity and less coke formation, was proved to be a potential catalyst for hydrocarbons production from chloromethane conversion. It is of particular interest that SAPO-34 gave an excellent performance in light olefins production from chloromethane transformation, which may be attributed to the shape selectivity and medium strong acidity of SAPO-34.

KEY WORDS: Chloromethane transformation; ZSM-5; SAPO-34; higher hydrocarbons; light olefins.

1. Introduction

Methane transformation to more useful higher hydrocarbons is one of the most important topics of natural gas utilization. During the past decades, although methane activation and its direct conversion to valuable compounds draw increasing attention, the successful processes are still in indirect pathway. Methane is transformed to syngas by partial oxidation or reforming, followed by a conversion to higher hydrocarbons using Fischer-Tropsch technology [1, 2]. In another process, syngas is converted firstly to methanol using Cu/ZnO/Al_2O_3 catalysts and then to hydrocarbons with MTG or MTO catalyst [3–6]. Even the Fischer-Tropsch process can produce higher hydrocarbons from syngas, the products always appeared in a long range. The complication of these routes also limits their economic interests. The development of alternative routes for higher hydrocarbon production through methane transformation attracts much attention from industry and academia.

In 1985, Olah et al. [7] reported a three-step process that methane could be converted to hydrocarbons via methyl halide. In his study methane could be directly converted to chloromethane by reacting with chlorine or hydrogen chloride and oxygen, then the produced chloromethane can be converted to hydrocarbons over zeolite catalyst. In 1988, C.E. Taylor et al. [8, 9] proposed a cyclic process for the conversion of methane to gasoline in a two-step process with chloromethane as intermediate. Chloromethane was produced through oxyhydrochlorination of methane in the first stage over a supported CuCl catalyst, and then, over a shape-selective zeolite, chloromethane was transformed to hydrocarbons in gasoline range and hydrogen chloride, which can be recycled to the first stage reaction. In 2000, C.E. Taylor [10] reported the further result that chloromethane can be converted to higher hydrocarbons over ZSM-5 and ZSM-11 zeolite catalysts at high conversion and stability and with aromatic and alkane as the main products. For the chloromethane transformation, among the zeolites used as catalysts, HZSM-5, with high activity and less coke formation, appeared to be the most promising catalyst [11–17]. Some modifications of ZSM-5 provided a further improvement on the activity and selectivity of the reaction [16, 18, 19]. Compared to the large series of works carried out over zeolites, the SAPO type molecular sieve catalysts, with excellent performance in catalytic conversion of methanol to light olefins [20–22], seemed to be neglected up to now in the research of chloromethane conversion. In regards the difference between zeolites and SAPO molecular sieves in the nature of the active sites, the activation and transformation of chloromethane on SAPO-34 should be quite different.

In the present study, zeolites and SAPOs with different porous structure and acid properties were employed as the catalysts for chloromethane transformation and their catalytic performances were tested and compared. The difference in conversion,

---

*To whom correspondence should be addressed.
E-mail: liuzm@dicp.ac.cn, bao-lian.su@fundp.ac.be

product distribution and coke formation from different porous structure and acidity of the catalysts were discussed.

2. Experimental

2.1. Catalyst preparation

ZSM-34 zeolite was synthesized by a hydrothermal method as described in the literature [23] from a gel composition of 80 Na_2O:80 SiO_2:1 Al_2O_3:15 K_2O:40 R:2800 H_2O, where R is 1,6 HDM as the template. The resulting gel was crystallized under auto-generous pressure at 16 °C. The synthesis of SAPO-34 and SAPO-5 followed the procedure reported in the literature [24, 25] with the starting gel composition of 1.0 Al_2O_3:1.0 P_2O_5:0.8 SiO_2:NEt_3:50 H_2O for SAPO-34 and 1.0 Al_2O_3:1.0 P_2O_5:0.2 SiO_2:3 NEt_3:50 H_2O for SAPO-5. The gels were sealed in the autoclave and the autoclave was heated at 200 °C for 15 h and 175 °C for 24 h under autogenetic pressure for SAPO-34 and SAPO-5 respectively. The products were filtrated, washed, and dried at 120 °C for 3 h. Other zeolites were commercial samples.

All the zeolite or SAPOs catalysts were evaluated in their protonic form. Ammonium from zeolites were prepared with ion-exchanged method with solution of ammonium nitrate. After the calcinations of ammonium form samples at 550 °C for 3 h, protonic form zeolites were obtained. For SAPOs, protonic form samples could be obtained directly with the template removing.

2.2. Characterization

The powder XRD patterns were recorded with a D/MAX-b X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5206$ Å). The chemical composition of the samples was determined with a Philips Magix X-Ray Fluorescence spectrometer. The textural data were obtained by nitrogen adsorption measurement using a Micromeritics 2010 analyzer.

The acidity of the calcined samples were determined by temperature programmed desorption of ammonia. 0.20 g calcined sample (40–60 mesh) were first activated at 650 °C for 30 min under a 40 ml/min of He flow. NH_3 was injected to saturate the samples at 100 °C. The measurement of desorbed of NH_3 was performed from 100 to 650 °C at a constant heating rate of 20 °C/min in a He flow of 40 ml/min.

The coke deposition of discharged catalysts was analyzed in air using a TA TGA2950 thermal analyzer. The sample was heated from room temperature to 800 °C with a heating rate of 10 °C/min.

2.3. Conversion of chloromethane

Chloromethane conversion was carried out in a fixed-bed quartz reactor at atmospheric 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. After the pretreatment, the temperature of reactor was adjusted to 400 °C for all the zeolite catalysts or 450 °C for SAPOs and the atmosphere was replaced by nitrogen and chloromethane (the molar ratio of N_2/CH_3Cl was 1). 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. Crystalline structure and textual properties of the catalysts

The XRD patterns of the as-synthesized ZSM-34, SAPO-5 and SAPO-34 molecular sieves are shown in figure 1. The position and the intensity of the diffraction peaks of the samples are identical to those reported in the literature [23–25]. Textual properties of all the catalysts samples after calcinations are given in table 1.

3.2. Temperature programmed desorption of ammonia

Temperature programmed desorption of ammonia is used to determine the acidity of the synthesized samples HZSM-34, SAPO-34 and SAPO-5, with the comparison of HZSM-5 and the profiles are given in figure 2. All the profiles consist of two distinct desorption peaks, correspond two kinds of acid sites with different strength. Among the four samples, NH_3 desorption from SAPO-5 occurs at lowest temperature 198 and 286 °C, and with lowest desorption amount, indicating its lowest acidity. SAPO-34, with desorption peak at 205 and 398 °C, which could be attributed to its weak and medium

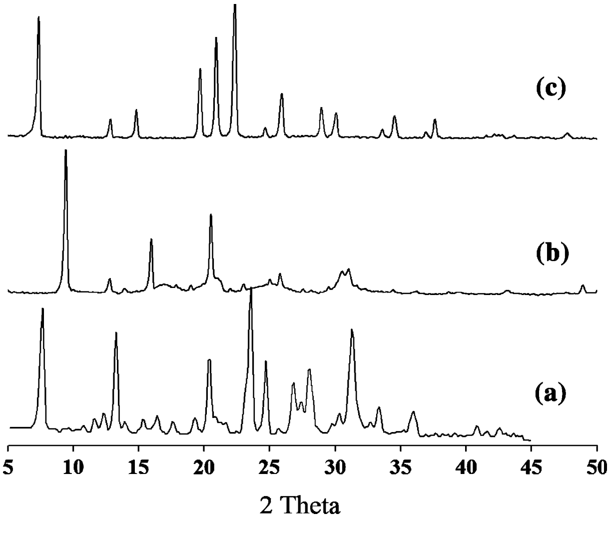

Figure 1. XRD patterns of synthesized samples. (a) ZSM-34; (b) SAPO-34; (c) SAPO-5.

Table 1
Chemical composition and textual properties of the catalysts

Catalyst	SO_2/Al_2O_3 mole ratio	Surface area m^2/g	Pore volume ml/g
HY	5.16	322.2	0.21
HBeta	25.72	425.2	0.40
HZSM-5	50.77	317.1	0.22
HMCM-22	23.85	360.1	0.39
HZSM-35	25.56	345.3	0.31
HZSM-34	7.50	303.1	0.22
SAPO-5	0.12	218.7	0.18
SAPO-34	0.25	433.0	0.24

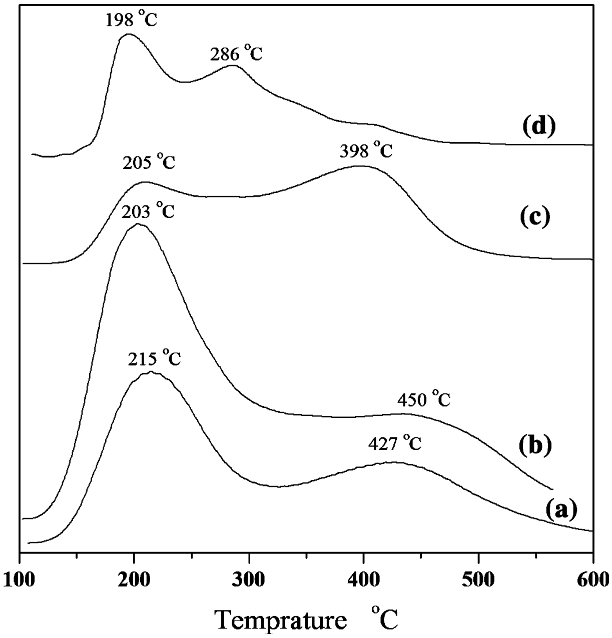

Figure 2. NH_3-TPD of synthesized samples. (a) ZSM-5; (b) ZSM-34; (c) SAPO-34; (d) SAPO-5.

strong acid sites. NH_3 desorption from HZSM-34, with desorption peak at 203 and 450 °C, appears in the similar temperature range as HZSM-5, demonstrating its strong acidity. The desorption at relatively high temperature may partly from the diffusion limitation of 8-ring pore structure of HZSM-34.

3.3. Catalytic performance

3.3.1. Chloromethane conversion

The catalysts with different pore structure, such as HY, HBeta, and SAPO-5 with 12-ring pore opening, HZSM-5, HMCM-22 and HZSM-35 with 10-ring pore opening, and HZSM-34 and SAPO-34 with 8-ring pore opening, were employed in the present study as the catalysts of chloromethane transformation. All the samples are in their protonic type, so their conversion will give the information of catalytic activity. From the catalytic performance over these acidic zeolites and molecular sieves listed in table 2, it can be found that the transformation over all the acidic zeolites, such as HY, Hbeta, HZSM-5, HMCM-22 and HZSM-35, chloromethane can be transformed to hydrocarbons with a relatively high chloromethane conversion. HZSM-5 and HZSM-34 are most active catalyst, with chloromethane conversion of 100% and 81% respectively. Other zeolites activity is lower than HZSM-5.

Framework structure of the zeolites has effects on the conversion and product distribution. When the conversion was carried out over HZSM-5 and HZSM-22, most of the chloromethane will be transferred to alkanes, toluene and xylene, this is similar to the catalytic performance of HZSM-5 in MTG process [26]. For HY and HBeta with 12-ring pore opening, C_4 and C_5 appear as the main, while for HZSM-34 with narrow pore opening, C_3H_8 formation becomes more remarkable. Some aromatic products can also be observed over HY, which may come from its cage structure. An exception observed is that over HZSM-35, chloromethane could be transferred to light alkenes, such as ethylene, propylene and butenes. This special selectivity may be caused by its relatively narrow and direct channel system, in which H-transfer reaction is hard to occur [28].

Over SAPOs molecular sieves, the conversion of SAPO-5 and SAPO-34 are about 20% and 50% respectively, indicating the relatively low activity compared to zeolite catalysts. The product obtained over SAPO molecular sieves is also quite different from the chloromethane conversion over zeolite catalysts. Chloromethane is mainly transferred to light alkenes over SAPO-5 and SAPO-34. For SAPO-5, 31% propylene and 14% butenes are obtained. While over SAPO-34, it is interesting find that most of the chloromethane are transformed to light alkenes, ethylene (25%), propylene (31%) and butenes (15%), indicating SAPO-34 is a very promising catalyst for light olefins production from chloromethane transformation.

3.4. Coke formation evaluated by TG

The coke deposition is observed for all the discharged catalysts of chloromethane transformation. Thermal analysis showed two weight losses (I and II) in the range of 25–800 °C for all the samples (figure 3). The first weight loss (I) in the range of 25–200 °C can be attributed to the water desorption from the samples. The

Table 2
Catalysis and thermogravimetric analysis performance of from chloromethane to hydrocarbons over various acid molecular sieve catalysts

Catalyst	HY	HBeta	HZSM-5	HMCM-22	HZSM-35	HZSM-34	SAPO-5	SAPO-34
Conversion (%)	44.82	50.56	99.93	54.27	45.02	81.45	20.19	50.61
Reaction temperature (°C)	400	400	400	400	400	400	450	450
Product distribution (%)								
CH_4	1.51	4.66	0.7	1.94	0.58	2.14	3.16	1.89
C_2H_4	13.23	6.98	1.51	4.51	12.09	7.59	9.08	24.72
C_2H_6	0.38	1.67	0.73	0.97	0.2	1.22	0.22	0.38
C_3H_6	3.48	0.72	1.66	1.31	14.06	5.54	31.46	31.4
C_3H_8	9.24	40.61	24.8	25.31	3.47	56.15	3.66	4.06
C_4H_8	0.92	0	0.95	0.53	19.16	2.82	14	15.09
C_4H_{10}	25.29	34.17	19.41	36.17	4.85	14.85	6.47	0.63
C_5^{+a}	25	11.18	23.91	17.49	32.8	8.35	30.68	21.57
Benzene	–	–	2.28	–	1.9	–	0.3	0.26
Toluene	19.72	–	9.52	11.77	8.75	0.24	0.36	–
Xylene	1.22	–	14.55	1	2.15	1.11	0.6	–
Coke wt%	10.5	8.8	1.6	7.3	4	10	0.6	3.3
Temperature range of coke removal (°C)	320–630	370–650	314–616	365–660	377–699	319–614	230–650	265–639

[a] Not include BTX.

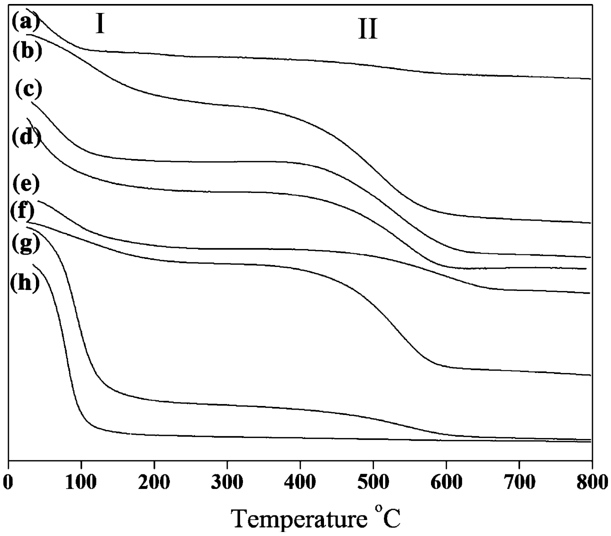

Figure 3. TG curves of various zeolites catalysts that reacted 2 h. (a) HZSM-5; (b) HY; (c) HBeta; (d) HMCM-22; (e) HZSM-35; (f) HZSM-34; (g) SAPO-34; (h) SAPO-5.

second weight loss (II) in the range of 200–700 °C corresponds to the coke removal. Detailed analysis given in table 2 showed that combustion of the coke species occurs in the different temperature range and the coke amount is also different.

For most of the zeolite catalysts studied here, such as HY, Hbeta, HZSM-34 and HMCM-22, more coke deposition is observed, but HZSM-35 and HZSM-5 showed lower coke formation. Some work in chloromethane transformation [15] has shown that the large pore zeolite catalysts, both in cationic and protonic form, such as X, Y, EMT, Beta, and MOR, in spite of their very interesting activity, led to the formation of large amount of coke in the chloromethane conversion due to the large size cages or channels present in these zeolites. While medium pore size ZSM-5 zeolite catalysts either in cationic or protonic form demonstrated their high activity and long life in the reaction and a strong reduction in the coke formation [13–15]. For the chloromethane transformation with hydrocarbons in gasoline range as target products, compared with other zeolite catalysts, HZSM-5 appeared to be the most promising catalyst, which has been also proved in the previous study [8–10].

In the present study, SAPO-5 and SAPO-34 gave a high selectivity for light olefins production, which is quite different from the products over zeolite catalyst. In the TG analysis, the coke formation during the transformation is also different from zeolite catalysts. Coke deposition is relatively low, with 3.3 wt% for SAPO-34 and only 0.65 wt% for SAPO-5. Coke removal is also found to occur in lower temperature range. Less coke formation may be from the mild acidity of SAPOs catalysts and the coke removal at low temperature indicates that coke species over SAPOs is different from zeolite and may be low-polymerized compared to zeolite catalysts.

4. Conclusions

A series of zeolite and SAPOs molecular sieves were synthesized and employed as catalysts for chloromethane transformation. Different catalytic performance may from the difference in porous structure and acidity. Over most zeolite catalysts, whose porous structure and stronger acidity favor the H-transfer reaction, alkanes and aromatics are main products, while over SAPOs catalyst with medium-strong or weak acidity, chloromethane is mainly transferred to light olefins. HZSM-5, with high activity and strong reduction in the coke formation, is a very promising catalyst for chloromethane conversion to higher hydrocarbons in gasoline range. It is also with particular interest to find that SAPO-34, is a potential catalyst for light olefins production with very high selectivity and low coke deposition.

References

[1] R.B. Anderson, *The Fischer-Tropsch synthesis* (Academic Press, New York, 1984).
[2] A.C. Vosloo, Fuel Proc. Technol. 71 (2001) 149.
[3] B.E. Leach, Appl. Industrial. Catal.Vol. 2, Academie press, 1983.
[4] M. Stocker, Micropor. Mesopor. Mater. 29 (1999) 3.
[5] C.D. Chang, Catal. Rev. –Sci. Eng. 25 (1983) 1.
[6] Z.M. Liu, C.L. Sun, G.G. Wang, Q.X. Wang and G.Y. Cai, Fuel Proc. Technol. 62 (2000) 161.
[7] G.A. Olah, B. Gupta, M. Farina, J.D. Felberg, M.P. Wai, A. Husain, R. Karpeles, K. Lammertsma, A.K. Melhotra and N.J. Trivedi, J. Am. Chem. Soc. 107 (1985) 7097.
[8] C.E. Taylor, R.P. Noceti and R.R. Schehl, Stud. Surf. Sci. Catal. 36 (1988) 483.
[9] C. E. Taylor, R. P. Noceti, Proc. Int. Congr. Catal. 9th Volume 2, 1988, p. 990.
[10] C.E. Taylor, Stud. Surf. Sci. Catal. 130 (2000) 3633.
[11] X.R. Xia, Y.L. Bi, T.H. Wu and K.J. Zhen, Catal. Lett. 33 (1995) 75.
[12] Z. Konya, I. Hannus and I. Kiricsi, Appl. Catal. B 8 (1996) 391.
[13] J. Denis and B.L. Su, Stud. Surf. Sci. Catal. 130 (2000) 1607.
[14] J. Denis and B.L. Su, Catal. Today 73 (2002) 187.
[15] J. Denis and B.L. Su, J. Mol. Catal. A 197 (2003) 263.
[16] L.A. Noronha, E.F. Souza-Aguiar and C.J.A. Mota, Catal. Today 101 (2005) 9.
[17] B. John, WO85/02608 (1985), to BP international limited.
[18] P. Lersch and F. Bandermann, Appl. Catal. 75 (1991) 133.
[19] Y. Sun, S.M. Campbell, J.H. Lunsford, G.E. Lewis, D. Palke and L.M. Tau, J. Catal. 143 (1993) 32.
[20] J. Liang, H.Y. Li, S.G. Zhao, W.G. Guo, R.H. Wang and M.L. Ying, Appl. Catal. 64 (1990) 31.
[21] I.M. Dahl, H. Mostad, D. Akporiaye and R. Wendelbo, Micropor. Mesopor. Mater. 29 (1999) 185.
[22] T. Inui and M. Kang, Appl. Catal. A 164 (1997) 211.
[23] J.C. Vartuli, G.J. Kennedy, B.A. Yoon and A. Malek, Micropor. Mesopor. Mater. 38 (2000) 247.
[24] X.S. Zhao, G.Q. Lu, A.K. Whittaker, J. Drennan and H. Xu, Micropor. Mesopor. Mater. 55 (2002) 51.
[25] S. Ashtekar and S.V.V. Chilukuri, et al. J. Phys. Chem. 98 (1994) 4878.
[26] C.D. Chang and A.J. Silvestri, J. Catal. 47 (1977) 249.
[27] J.F. Haw, W.G. Song, D.M. Marcus and J.B. Nicholas, Acc. Chem. Res. 36 (2003) 317.