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Electrophilic chlorination of methane over superacidic sulfated zirconia ☆

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Catalytic chlorination of methane was studied over SO_4^{2-}/ZrO_2, $Pt/SO_4^{2-}/ZrO_2$, and $Fe/Mn/SO_4^{2-}/ZrO_2$ solid superacid catalysts. The reactions were carried out in a continuous flow reactor under atmospheric pressure, at temperatures below 240°C, with a gaseous hourly space velocity of 1000 ml/g h and a methane to chlorine ratio of 4 to 1. At 200°C with 30% chlorine converted the selectivity in methyl chloride exceeds 90%. At more elevated temperatures, the selectivity decreases but stays above 80% in methyl chloride at 225°C using the sulfated zirconia catalysts. The selectivity can be enhanced by adding platinum to sulfated zirconia catalysts. An iron and manganese-doped catalyst exhibited excellent selectivities at somewhat lower conversions. Methyl chloride is obtained at 235°C in selectivities greater than 85%. No chloroform or carbon tetrachloride is formed. The electrophilic insertion involves electron-deficient metal-coordinated chlorine into the methane C–H bond.

Keywords: Methane; chlorination; solid superacids; sulfated zirconia

1. Introduction

Activation of methane is a field of intensive research activity. Electrophilic conversions [1,2] are promising possibilities since they provide feasible routes to selective transformation of methane to higher hydrocarbons and to selective monofunctionalization [1]. Radical reactions, in contrast, are rather non-selective. An important approach, the oxidative coupling of methane, has been studied extensively [3–6]. Although significant improvements have been achieved, it is still far

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☆ Catalysis by solid superacids, 29. For part 28 see ref. [14].

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from industrial application. Radical chlorination of alkanes possessing different carbon–hydrogen bonds yields all possible monochlorinated isomeric products [7–9] whereas chlorination of hydrocarbons with a single type of carbon–hydrogen bond, such as methane, leads to a mixture of mono- and polychlorinated products. Using conventional methane chlorination large excess of methane is needed (methane to chlorine ratio of at least 10 to 1) to produce selectively methyl chloride in radical reactions (thermal or photochemical) [10]. The selective catalytic monochlorination of methane, therefore, remains a significant subject of investigations since still no proven commercial process is available.

Methane chlorination is catalyzed in solution by $[PtCl_4]^{2-}$ systems [11]. The Pt(II) complex activates the C–H bond of methane and the electrophilic insertion into the platinum complex proceeds through a methylplatinum intermediate. Further oxidative chlorination by Pt(IV) yields methyl chloride. Under superacidic conditions methane reacts with SbF_5/Cl_2 in SO_2ClF at −78°C to give methyl chloride in high selectivity but the conversion is very low [12]. No other chloromethanes are observed. Catalytic heterogeneous gas-phase chlorination of methane has also led to methyl chloride with high selectivity. Methyl chloride was obtained in selectivities greater than 96% in a continuous flow system over solid superacids such as TaF_5/Nafion-H, SbF_5/graphite or with supported noble metals like Pt/Al_2O_3, and $Pd/BaSO_4$ [13]. No chloroform or carbon tetrachloride was observed. Zeolites have also been investigated as catalysts for the chlorination of methane [14]. They show high initial selectivity ($\sim$ 100%) in methyl chloride above 325°C but lose their selectivity after 5 h on stream due to aluminum extraction from the framework of the zeolite by hydrogen chloride. Zeolites with higher acidity gave better selectivity at lower temperature. It was suggested that in the presence of chlorine molecules Brønsted sites of zeolites are transformed to chlorooxonium ion sites where the de facto electrophilic chlorination takes place. These studies showed that strong acidic catalysts promote electrophilic chlorination of methane at relatively low temperature. Hydrogen chloride formed as by-product of the chlorination affects the life time of the catalysts.

Sulfate containing metal oxides are known to be solid superacids used in various reactions (cracking, isomerization, alkylation, acylation, esterification, polymerization, oligomerization, oxidation) [15]. Amongst the metal oxides zirconia showed the highest acidity strength ($H_0 = -16$ determined with Hammett indicators) [16]. A recent study of the sulfated zirconia using a spectrophotometric method showed that its surface acidity is $H_0 \approx -12$ [17]. Addition of platinum [18] or iron and manganese on these precursors gives more active solids [19].

Now our studies show that sulfur promoted zirconium oxide solid superacids selectively catalyze the electrophilic chlorination of methane at temperatures below 240°C. The influence of the addition of metal ions to sulfated zirconia in the chlorinations was also studied.

2. Experimental

2.1. PREPARATION OF CATALYSTS

The catalysts used are presented in table 1. The sulfated zirconia catalysts were prepared as follows. $ZrOCl_2 \cdot 8H_2O$ or $ZrO(NO_3)_2 \cdot xH_2O$ (from Aldrich) was hydrolyzed with excess of 28% aqueous ammonia to reach pH 10.5. The precipitate was washed with distilled water, dried at 110°C overnight to obtain $Zr(OH)_4$ and impregnated with an appropriate amount of a 0.5 M solution of $(NH_4)_2SO_4$ to achieve the given nominal loadings (4, 6, 9, or 15 wt%) of sulfate ions and then evaporated to dryness. The solids were calcined under air flow by raising the temperature at a rate of 3.3°C/min to 575 or 600°C, and maintained at that temperature for 3 h.

Platinum was loaded into the sulfated zirconium hydroxide previously dried at 110°C by impregnation with a solution of $H_2PtCl_6 \cdot xH_2O$. The precursor was dried and calcined at 600°C for 3 h under air flow.

1.5 wt% Fe/0.5% Mn/4% SO_4^{2-}/ZrO_2 was obtained by impregnating dried $Zr(OH)_4$ with 0.25 M $Fe(NO_3)_3$, 0.1 M $Mn(NO_3)_2$, and 0.5 M $(NH_4)_2SO_4$ solutions, respectively, calcining the precursor at 725°C for 1.5 h under air flow.

2.2. REACTANTS

The reactants used were methane (UN-1971) with minimum purity of 99.0% and chlorine (UN-1017-RQ) with minimum purity of 99.5% both purchased from Matheson.

2.3. REACTOR AND EXPERIMENTS

Experiments were performed in a fixed-bed, continuous flow reactor

Table 1
Catalysts used

Catalyst	Source material	Calc. temp. (°C)	Pretreat. temp. (°C)
$X\%\ SO_4^{2-}/ZrO_2\ (X = 4, 9, 15)$	$ZrOCl_2 \cdot 8H_2O$	600	350
6% SO_4^{2-}/ZrO_2	$ZrO(NO_3)_2 \cdot xH_2O$	575	350
$Y\%\ Pt/X\%\ SO_4^{2-}/ZrO_2$ $((Y, X) = (0.5, 8)$ or $(1.5, 4))$	$ZrOCl_2 \cdot 8H_2O$ $H_2PtCl_6 \cdot xH_2O$	600	350
1.5% Fe/0.5% Mn/4% SO_4^{2-}/ZrO_2	$ZrOCl_2 \cdot 8H_2O$ $Fe(NO_3)_3 \cdot 9H_2O$ $Mn(NO_3)_2$ 50% sol.	725	450

(400 × 12 mm pyrex glass tube) operating under atmospheric pressure and electrically heated with a Thermolyne furnace. The pathway of chlorine was shielded from light.

In all the experiments about 3 g of catalyst was loaded in the reactor and pretreated for 1 h in a flow of air prior to the reaction. The pretreatment temperature was 450°C for the sulfated zirconia doped with iron and manganese, and 350°C for the other catalysts.

The reactor was then set at the reaction temperature and fed with methane and chlorine at a gaseous hourly space velocity of 1000 ml/g h. The products were analyzed by GC using a 30 DB-1 capillary column and a flame ionization detector.

3. Results and discussion

The results of the heterogeneous catalytic chlorination of methane carried out between 200 and 235°C over zirconium oxide loaded with 4, 6, 9, and 15% SO_4^{2-} (at a GHSV of 1000 ml/g h) are shown in table 2. From these data it can be seen that conversion (based on chlorine) increases with increasing temperature while selectivity decreases. These results contrast those over zeolite catalysts. Bucsi and Olah [14] working with various zeolites showed that both selectivity and conversion increase with temperature and selective monochlorination occurred even above 325°C.

Table 2
Chlorination of methane over SO_4^{2-}/ZrO_2 catalysts (CH_4/Cl_2 4 : 1)

Catalysts X% SO_4^{2-}/ZrO_2	React. temp. (°C)	React. time (h)	Conversion [a] (%)	Product distribution (%)		
				CH_3Cl	CH_2Cl_2	$CHCl_3$
$X = 4$	200	6	31	91	9	
	225	7	59	82	18	trace
	225 [b]	7	55	83	17	trace
$X = 6$	200	7	27	91	9	
	225	7	44	86	14	
$X = 9$	200	5	29	92	8	
	225	7	69	80	20	<0.4
	235	4	95	70	27	2 [c]
$X = 15$	235	1	91	72	26	2
		5	80	75	24	1

[a] Based on chlorine. Conversion is averaged over the duration of the experiment where changes do not exceed 3%.

[b] Calcined at 650°C.

[c] 1% ethane was observed.

Table 2 also shows that at 200°C, the conversions are about 30% with selectivities of 91–92% in methyl chloride. Neither chloroform nor carbon tetrachloride is detected. The amount of sulfate ions on zirconium oxide had little effect on the activity of the catalysts.

At 225°C the selectivity is 80–86% in methyl chloride, the balance being methylene chloride. Traces of chloroform are observed. 4% SO_4^{2-}/ZrO_2 catalysts calcined at 600 and 650°C showed identical selectivity. However, the conversion is somewhat higher for the former. The catalyst with 6% SO_4^{2-} calcined at 575°C showed the highest selectivity in methyl chloride (86%). Comparing the catalysts containing 4% SO_4^{2-} and 9% SO_4^{2-} made from the same starting material and calcined at the same temperature (see table 1), an increase in the conversion from 59 to 69% was observed by increasing the sulfate ion content, the product distribution in both cases remained very close.

At 235°C the conversion of chlorination is 95% with methyl chloride obtained in 70% yield, with 27% methylene chloride and 2% chloroform. The activity of 15% SO_4^{2-}/ZrO_2 decreased gradually with time. The conversion dropped from 91 to 80% after 5 h on-stream, but the product distribution practically remained unchanged. In fact, sulfated zirconia exhibits superacidity with sulfate contents ranging from 1 to ~ 8% [18]. The surface activity of the sulfate-containing metal oxides depends on the type of reaction, the sulfate source, the amount of sulfate ions, the calcination temperature, and starting material [15,16,18,20,21].

Table 3 summarizes data on the chlorination of methane over sulfated zirconia loaded with platinum or iron and manganese. Surprisingly, these catalysts are less active than the metal-free sulfated zirconia catalysts. However, their selectivity in methyl chloride is substantially improved. It is worth to mention that, in contrast to metal-free sulfated zirconia catalysts, chloroform and carbon tetrachloride were not formed even at 235°C. The selectivity in methyl chloride was enhanced by treat-

Table 3
Chlorination of methane over supported metal sulfated zirconia catalysts (CH_4/Cl_2 4 : 1)

Catalysts	React. temp. (°C)	React. time (h)	Conversion[a] (%)	Product distribution (%)	
				CH_3Cl	CH_2Cl_2
1.5% Pt/4% SO_4^{2-}/ZrO_2	210	7	27	93	7
	235	7	60	81	19
	235[b]	5	50	86	14
0.5% Pt/8% SO_4^{2-}/ZrO_2	235	5	43	88	12
1.5% Fe/0.5% Mn/ 4% SO_4^{2-}/ZrO_2	200	7	5	100	
	215	7	12	99	1
	235	7	39	90	10

[a] Based on chlorine.

[b] Reduced at 175°C for 1 h, $CH_4/Cl_2/H_2$ 4.3 : 1 : 1, GHSV 1260 ml/g h.

ing the 1.5% Pt/4% SO_4^{2-}/ZrO_2 catalysts in hydrogen. Also, 0.5% Pt/8% SO_4^{2-}/ZrO_2 containing less platinum and more sulfate ions is slightly more selective than 1.5% Pt/4% SO_4^{2-}/ZrO_2. Pt/SO_4^{2-}/ZrO_2 catalysts were shown to exhibit higher activity as well as long lifetime for pentane isomerization in presence of hydrogen [22]. It was proposed that the dissociation of hydrogen on Pt results in the formation of Brønsted acid sites. Among all the catalysts studied, 1.5% Fe/0.5% Mn/4% SO_4^{2-}/ZrO_2, known as the most active non-halide solid for butane isomerization [19], was found to be the least active, but the most selective for the chlorination of methane. This catalyst was almost inactive at 200°C with only 5% conversion and gave 40% conversion at 235°C with 90% methyl chloride. As already mentioned, no chloroform or carbon tetrachloride was observed.

All catalysts maintained their activity during the experimental runs except 15% SO_4^{2-}/ZrO_2. If not noted otherwise (see tables 2–4), traces of ethane were observed. At 235°C, brownish-red deposits (sublimation of $FeCl_3$ and $MnCl_2$) were observed at the bottom end of the reactor after the reaction with 1.5% Fe/0.5% Mn/4% SO_4^{2-}/ZrO_2 catalyst. A slight yellowish deposit at 225°C, more intense at 235°C was also observed with the other catalysts.

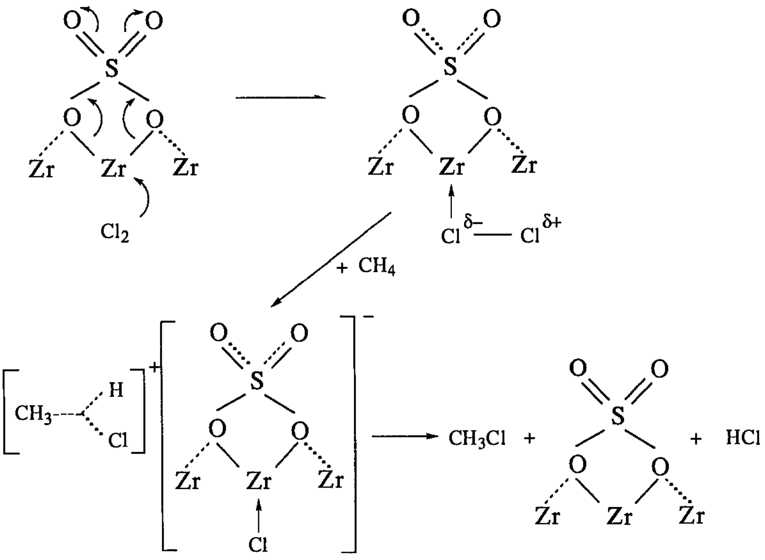
The effect of the methane to chlorine ratio over 9% SO_4^{2-}/ZrO_2 was investigated at 225 and 235°C, with a GHSV of 1000 ml/g h. The results are presented in table 4. It can be seen that at 225°C product distributions are almost identical for CH_4/Cl_2 ratios of 6 : 1 and 8 : 1 and only slightly different for CH_4/Cl_2 ratio of 4 : 1. No chloroform or carbon tetrachloride were formed for CH_4/Cl_2 ratios higher than 4 : 1. At 235°C the product distribution is significantly different with CH_4/Cl_2 ratios of 4 : 1 to 7 : 1. No chloroform or tetrachloride is produced in the latter. Significant changes in product distributions with the methane to chlorine ratios are characteristic of radical reactions. Although free radical reaction cannot be completely ruled out at 225°C, it decisively seems more important at 235°C.

The strong acidity of the zirconium cation in sulfated zirconia is due to the inductive effect of the S=O or  bonds in the sulfur complex [18,21,23,24] (scheme 1). The chlorination mechanism might be identical to that previously sug-

Table 4
Effect of CH_4/Cl_2 ratios on the chlorination of methane over 9% SO_4^{2-}/ZrO_2 catalyst

CH_4/Cl_2	React. temp. (°C)	Conversion[a] (%)	Product distribution (%)		
			CH_3Cl	CH_2Cl_2	$CHCl_3$
4 : 1	225	69	80	20	<0.4
6 : 1	225	76	86	14	
8 : 1	225	88	87	13	
4 : 1	235	95	70	27	2[b]
7 : 1	235	97	85	15	

[a] Based on chlorine.
[b] 1% ethane was observed.



Scheme 1.

gested by Olah et al. [13] for the halogenation of methane over oxyhalide or supported Lewis superacid catalysts. Cl_2 is polarized at the Lewis centers of the catalysts and chlorination of methane takes place under electrophilic conditions (scheme 1. For the sake of simplicity only the $\mathrm{S}{\lessgtr}^{\mathrm{O}}_{\mathrm{O}}$ bond structure suggested by Tanabe et al. [18] is shown).

With Pt/SO_4^{2-}/ZrO_2 solids an additional mechanism similar to the mechanism suggested by Olah et al. [13] for the halogenation of methane over Pt/Al_2O_3 could take place. Electrophilic insertion by Pt(II) chloride, however, cannot be excluded. Dichloromethane or chloroform is formed by further chlorination of methyl chloride and methylene chloride, respectively. The presence of chloroform (no carbon tetrachloride was observed) does not exclude the possibility of free radical reaction initiated by hydrogen abstraction competing with the electrophilic insertion. Below 250°C chlorination of methane over glass powder (radical reaction) is however negligible [14]. Olah and Houk [1] have shown that the energy difference between the singlet–triplet state of positive halogens favors the electrophilic halogenation of methane but the complexity of the system may involve radical ions even under conditions where radical reactions are not expected [25].

In conclusion, the electrophilic chlorination of methane catalyzed by sulfated zirconia at temperatures below 225°C gives a selectivity of greater than 80% in methyl chloride. Above 225°C chloroform is formed, but no carbon tetrachloride is observed. Addition of metal ions to sulfated zirconia improves methyl chloride selectivity but the conversion is lower. No chloroform or carbon tetrachloride is formed even at 235°C. Although the catalysts maintained their activity (except 15% SO_4^{2-}/ZrO_2) over the usually experimental 5–7 h, metal chlorides are slowly removed at 225°C and above from the solids by hydrogen chloride as indicated by deposit formation at the end of the reactor tube. The electrophilic chlorination is considered to proceed by insertion of a zirconium-coordinated electrophilic chlorine species or/and electron-deficient metal into the methane C–H bond followed by chlorinolitic cleavage to give methyl chloride. Subsequent reaction of methyl chloride gives methylene chloride.

References

[1] G.A. Olah, Accounts Chem. Res. 20 (1987) 422, and references therein.

[2] G.A. Olah and G.K.S. Prakash, in: *The Chemistry of Alkanes and Cycloalkanes*, eds. S. Patai and Z. Rappoport (Wiley, Chichester, 1992) p. 624.

[3] J.S. Lee and S.T. Oyama, Catal. Rev.-Sci. Eng. 30 (1988) 249.

[4] G.J. Hutchings, M.S. Scurrell and J.R. Woodhouse, Chem. Soc. Rev. 18 (1989) 251.

[5] Y. Amenomiya, V.I. Birss, M. Goledzinowski, J. Galuszka and A.R. Sanger, Catal. Rev. -Sci. Eng. 32 (1990) 163.

[6] E.E. Wolf, ed. *Methane Conversion by Oxidative Processes: Fundamental and Engineering Aspects* (Van Nostrand Reinhold, New York, 1992).

[7] E.S. Huyser, in: *The Chemistry of the Carbon–Halogen Bond*, ed. S. Patai (Wiley, London, 1973) p. 549.

[8] M.L. Poutsma, in: *Free Radicals*, Vol. 2, ed. J.K. Kochi (Wiley, New York, 1973) p. 159.

[9] M. Hudlicky and T. Hudlicky, in: *The Chemistry of Functional Groups*, Suppl. D, eds. S. Patai and Z. Rappoport (Wiley, Chichester, 1983) p. 1021.

[10] N.K. Chaney, Ind. Eng. Chem. 11 (1919) 420;
G.W. Jones and V.C. Allison, Ind. Eng. Chem. 11 (1919) 639;
K. Weissermel, H.-J. Arpe, in: *Industrial Organic Chemistry* (VCH, Weinheim, 1993) p. 50.

[11] J.R. Saders, D.E. Webster and P.B. Wells, J. Chem. Soc. Dalton Trans. (1975) 1191;
J.L. Garnett and J.C. West, Aust. J. Chem. 27 (1974) 29;
V.P. Tretyakov, G.P. Zimtseva, E.S. Rudakov and A.N. Osebkii, React. Kinet. Catal. Lett. 12 (1979) 543;
I.T. Horvath, R.A. Cook, J.M. Millar and G. Kiss, Organometallics 12 (1993) 7686.

[12] G.A. Olah and Y.M. Mo, J. Am. Chem. Soc. 74 (1972) 6864;
G.A. Olah, R. Renner, P. Schilling and M.K. York, J. Am. Chem. Soc. 95 (1973) 7686.

[13] G.A. Olah, B. Gupta, M. Farina, J.D. Felberg, W.M. Ip, A. Husain, R. Karpeles, K. Lammertsma, A.K. Melhotra and N.J. Trivedi, J. Am. Chem. Soc. 107 (1985) 7097.

[14] I. Bucsi and G.A. Olah, Catal. Lett. 16 (1992) 27.

[15] K. Arata, Adv. Catal. 37 (1990) 165, and references therein.

[16] M. Hino and K. Arata, J. Chem. Soc. Chem. Commun. (1980) 851.

[17] B. Umansky, J. Engelhardt and W.K. Hall, J. Catal. 127 (1991) 128.

[18] K. Tanabe, H. Hattori and T. Yamaguchi, Crit. Rev. Surf. Chem. 11 (1990) 1, and references therein.

[19] C.-H. Lin and C.-Y. Hsu, J. Chem. Soc. Chem. Commun. (1992) 1479;
C.-Y. Hsu, C.R. Humbuch, C.T. Armes and B.C. Gates, J. Chem. Soc. Chem. Commun. (1992) 1645.

[20] F.R. Chen, G. Coudurier, J.-F. Joly and J.C. Vedrine, in: *Symp. Alkylation, Aromatizaton, Oligomerization, and Isomerization of Short Chain Hydrocarbons over Heterogeneous Catalysts*, New York 1991, pp. 878.

[21] C. Morterra, G. Cerrato, C. Emanuel and V. Bolis, J. Catal. 142 (1993) 349.
[22] K. Ebitani, J. Konishi, A. Horie, H. Hattori and K. Tanabe, in: *Acid–Base Catalysts*, eds. K. Tanabe, H. Hattori, T. Yamaguchi and T. Tanabe (Kodansha/Verlag-Chemie, Tokyo/Weinheim, 1989) p. 491.
[23] T. Jin, T. Yamaguchi and K. Tanabe, J. Phys. Chem. 90 (1986) 4794.
[24] M. Bensitel, O. Saur and J.-C. Lavalley, Mater. Chem. Phys. 19 (1988) 148.
[25] N. Kitajima and J. Schwartz, J. Am. Chem. Soc. 106 (1984) 2220.