JOURNAL OF CATALYSIS 97, 511–515 (1986)

Zr-Containing Pillared Interlayer Clays

II. Catalytic Activity for the Conversion of Methanol into Hydrocarbons

R. BURCH[1] AND C. I. WARBURTON

Department of Chemistry, The University of Reading, Whiteknights, Reading RG6 2AD, United Kingdom

Received January 21, 1985; revised September 17, 1985

Zr-Containing pillared interlayer clays have been prepared by reaction of zirconyl chloride solutions with washed montmorillonite clays. The catalytic properties have been determined for the conversion of methanol into hydrocarbons in a flow microreactor at atmospheric pressure. The results show that the selectivity of the various samples is essentially independent of the method preparation. The major products are C_2–C_4 olefins, which are formed with a selectivity of about 65%. The activity, however, is critically dependent on the method of preparation. It is found that the activity decreases rapidly as the surface area of the samples is increased. Possible reasons for this unusual effect are discussed. © 1986 Academic Press, Inc.

INTRODUCTION

Zeolites represent one of the most versatile and important classes of catalytic material. They are highly acidic and can catalyse, for example, dehydration reactions. They can also influence the selectivity of a catalytic process because of the physical constraints imposed by the dimensions of the zeolite channels. One of the best known recent applications of zeolites is the use of ZSM-5 to convert methanol into gasoline or lower olefins (*1, 2*). Inorganic hydroxy compounds of Al (*3–13*) and Zr (*4, 5, 13, 14*) have been used to prepare zeolite-type materials from layer clay structures. In Part I (*15*) we have described the preparation of Zr-containing pillared interlayer clays (Zr-PILC) and have shown how the structure and physical properties of the PILC are affected by the method of preparation. These PILC materials are also acidic and contain narrow channels between the clay layers. Kikuchi *et al.* (*13*) have demonstrated for a single Zr-containing PILC that quite high activity and selectivity for the conversion of methanol into C_2–C_4 olefins is possible.

The objective of the work described in the present paper was to extend the earlier work and to investigate the interrelationship between the structural and physical properties of Zr-PILC and their catalytic properties for the conversion of methanol into hydrocarbons.

EXPERIMENTAL METHODS

1. Preparation of PILC. Full details of the different methods of preparation used have been given in Part I (*15*), together with details of the measurement of surface areas, and Zr analysis. XRD patterns showed that PILC prepared from washed clay were more homogeneous than those prepared from the as-received clay. Consequently, catalytic experiments have been performed only on samples prepared from washed clay. Table 1 gives details of the methods of preparation used, of the surface areas obtained, and of the Zr contents of the samples used in the catalytic work.

2. Catalytic measurements. The activity and selectivity of the catalysts was determined for the conversion of methanol into hydrocarbons under continuous flow conditions in an atmospheric pressure, all-glass microreactor. The samples were calcined for 16 h at 673 K and a portion (0.200 g) loaded into the glass reactor which was coupled through ball and socket joints to a stainless-steel gas manifold. Pretreatment

---

[1] To whom correspondence should be addressed.

0021-9517/86 $3.00

TABLE 1

Details of Preparation, Surface Area, and Zr Content of PILC

Sample	State of Zr solution[a]	Ageing temperature (K)	Ageing time (h)	Surface area[b] ($m^2\ g^{-1}$)	Zr (wt%)
W2	U	290	1	153	8.6
W3	U	340	1	254	13.6
W4R	R	290	1	214	13.2
W5	U	290	24	176	9.2
W6	U/0.05	290	1	153	8.5
W7	U	273	1	132	6.8
WF8[c]	U	290	1	148	8.1

[a] U indicates unrefluxed 0.1 *M* zirconyl chloride solution R indicates 0.1 *M* zirconyl chloride solution refluxed for 24 h U/0.05 indicates unrefluxed 0.05 *M* zirconyl chloride solution.

[b] After heating in air for 16 h at 673 K.

[c] F indicates that only a fine fraction of the clay was used.

involved heating in N_2 at 673 K for 2 h at a gas flow of 6 $dm^3\ g^{-1}\ h^{-1}$.

Methanol (0.8 $cm^3\ h^{-1}$) was injected from a motor-driven syringe into a stream of N_2 (6 $dm^3\ g^{-1}\ h^{-1}$) and the mixture passed through the catalyst which was heated by a small electric furnace. Products were analysed by gas chromatography, the separation being achieved by using a composite column of Poropak P (2 m) + Poropak Q (3 m), operated at 373 K for 9 min, then programmed to 433 K at 6 K min^{-1}. The signal from the FID detector of the GC was integrated electronically. Product distributions are given as weight percentage, and the activity is given as the wt% methanol converted into products, either total products (including dimethyl ether, C_T) or into hydrocarbon products (C_H).

RESULTS

The conversion of methanol into hydrocarbons involves two distinct stages. Dehydration occurs first with the formation of dimethyl ether, and this reaction proceeds even on the external surfaces of the clay. The dimethyl ether is then further dehydrated to give hydrocarbon products. This reaction only proceeds on acidic sites situated between the layers of the clay structure. Formation of PILC opens up the interlayer region and makes acidic sites accessible to the dimethyl ether.

With our PILC there is a decline in activity initially but in most cases the activity changes only slowly after about 3 h on stream. We have chosen the activity after 3 h on stream as being representative of the activity of a particular sample. The optimum temperature for the formation of C_2–C_4 olefins was found to lie in the range 623–673 K. To facilitate comparison with the results reported by Kikuchi *et al.* (*13*) we have chosen 623 K as a standard test temperature.

Influence of Method of Preparation on the Activity and Selectivity

Kikuchi *et al.* (*13*) prepared and reported data for a single Zr-PILC. Table 2 shows our results for seven different preparations. The activity for the conversion to hydrocarbons ranges over 2 orders of magnitude. The highest activity is observed for samples (W2, W7) prepared using unrefluxed Zr chloride solutions and aged for 1 h at low temperatures. The lowest activity is found with samples (W3, W4R) where the ageing temperature is raised, or the Zr chloride solution is refluxed prior to addition of the

TABLE 2

Influence of Method of Preparation on the Activity and Selectivity of Various PILC[a]

Sample	W2	W3	W4R	W5	W6	W7	WF8
C1	2.18	77.8	15.3	4.86	3.66	2.84	2.54
$C2^=$	15.4	22.2	18.7	21.5	20.8	17.4	17.1
C2	0.28	nd[b]	nd	nd	nd	0.55	0.36
$C3^=$	22.5	nd	30.1	32.2	31.5	23.5	23.8
C3	0.16	nd	nd	nd	0.39	0.41	0.34
$C4^=$	27.0	nd	29.7	19.0	16.8	20.9	20.7
C4	14.9	nd	6.26	12.4	16.6	14.6	14.3
$C5_+$	17.6	nd	nd	10.1	10.3	19.8	20.9
C_T	69.7	77.2	75.4	98.7	77.9	41.6	39.1
C_H	13.2	0.15	0.81	2.54	5.88	14.4	8.46
S_{2-4}	64.9	22.2	78.5	72.6	69.1	61.8	61.6

[a] Conditions were: heated for 2 h in N_2 at 673 K, tested at 623 K, and data taken after 3 h on stream.

[b] None detected.

clay. Intermediate behaviour is exhibited by samples in which the ageing time is increased (W5) or when the concentration of Zr chloride is reduced (W6).

These activity data fit a consistent pattern. The samples prepared from solutions in which the minimum amount of polymerisation of the Zr tetramers has occurred have by far the highest activity.

The selectivity data shown in Table 2 for the more active catalysts indicate that there is only a minor influence of the method of preparation. For these catalysts the selectivity to C_2–C_4 olefins is close to 65% although the proportions of C_2, C_3, and C_4 olefins do vary somewhat.

Effect of Water Vapour on Activity and Product Distribution

Water is produced in the methanol reaction. It is known (*16*) that in the case of zeolite catalysts the selectivity for the formation of olefins may be affected by the partial pressure of water vapour. Figure 1 shows the effect of adding water (30% v/v) to the methanol feed. The activity for the formation of hydrocarbons drops by about 40% when water is added. Replacement of the water/methanol mixture with pure methanol results in the recovery of most of the original activity. These changes in activity are repeated when the feedstock is alternated between dry and wet methanol.

The selectivity for the formation of C_2, C_3, and C_4 olefins follows the changes in activity. When water is added the selectivity for the formation of C_2 and C_3 olefins is increased at the expense of C_4 olefins. This trend towards the formation of shorter C–C chains is paralleled by the decrease in the % C_{5+} hydrocarbons produced, as is also shown in Fig. 1. In zeolites this increase in selectivity for the formation of light olefins has been attributed to a deactivation of the strongly acidic sites by water (*17*). These sites are believed (*18*) to be responsible for the further reaction of light olefins to produce aromatics. The actual increase in light olefin selectivity observed in the present work with PILC is less than that observed with some zeolites (*19*). This probably reflects the fact that the PILC already have lower acidities than zeolites so the capacity for improving the selectivity is limited.

Effect of Surface Area on Catalytic Activity

Figure 2 shows the variation in activity of our catalysts as a function of the apparent

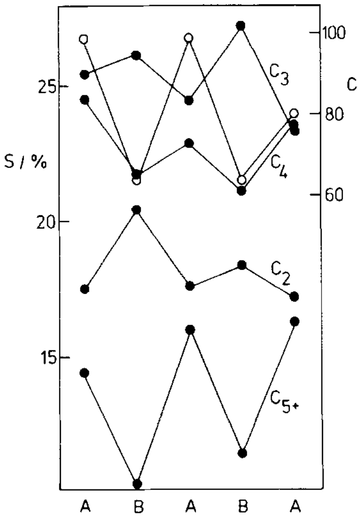

FIG. 1. Effect of adding water to the methanol feed on the total activity C_T (open circles), and the selectivity to C_2, C_3, or C_4 olefins or to C_{5+} products. A indicates pure methanol feed; B indicates feed containing 30% water.

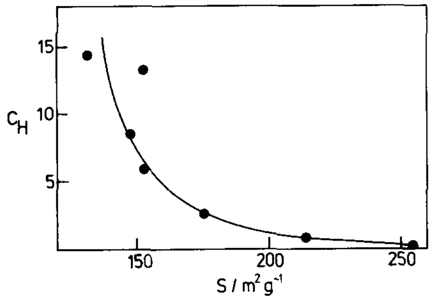

FIG. 2. Variation in activity for the formation of hydrocarbons from methanol as a function of BET surface area of various PILC.

surface area of the fresh sample after calcination at 673 K for 16 h.

The activities decline very rapidly as the surface area is increased. The activity per unit area decreases by a factor of 200 when the surface area is increased from 140 to 250 m^2 g^{-1}.

DISCUSSION

In their work on PILC Kikuchi *et al.* (*13*) reported that the activity for the conversion of methanol into olefins decreased as the interlayer spacing decreased. We have observed exactly the opposite trend. (The surface areas of our samples are closely related to the interlayer spacing.) We believe that the discrepancy arises because Kikuchi *et al.* compared the activity of PILC prepared using different pillaring ions and assumed that the nature of the pillaring species was unimportant. In fact it is clear from their results that this is not correct. Thus the interlayer spacings for Cu, Zn, Si, and Cr PILC are, respectively, 0.54, 0.57, 0.45, and 0.30 nm. The activity, however, decreases, in the order Si > Cr > Zn = Cu, with the last two materials being totally inactive.

The inverse relationship observed in the present work between surface area and activity could be due either to changes in the acidity or the physical structure of the PILC as the method of preparation is varied.

Differences in catalytic activity due to variations in acidity could arise for different reasons depending on whether the active site is situated on the inner clay layers, on the pillars themselves, or at the point of contact between the clay and the pillar. If the acidity is only due to the clay then a loss of activity could occur if sites are blocked or shielded by the pillaring species. On the other hand if the active acidic sites are associated with the pillars changes in the stoichiometry of the pillars could affect the activity. The fact that for the different catalysts the product distribution hardly changes suggests that it is the number rather than the nature of the active sites which is varying.

It is also possible that the physical dimensions of the cavities in a PILC affect the activity. Whereas in a zeolite the reactant molecule in a cavity may be acted upon by the force field of several acidic sites simultaneously, in a PILC most of the internal surface will be either nonacidic or only weakly acidic. Consequently, if the cavity is much larger than the dimensions of a reactant molecule the activity of an acidic site will be equivalent to that of a comparable site on the external surface of the clay. However, if the cavity is just large enough for the reactant molecule to diffuse in the activity could be greatly enhanced due to an increase in the number of successful molecule-active site collisions (*20*).

In conclusion, our experiments have shown that the activity of Zr-PILC for the dehydration of methanol is dependent on the method of preparation. There is an inverse relationship between the activity and the surface area of the PILC. At this stage it is not known whether this reflects differences in the acidity or in the physical dimensions of the materials.

ACKNOWLEDGMENTS

We are grateful to Magnesium Elektron Ltd. for sponsoring this research and to the SERC for awarding a CASE studentship to C.I.W. We are pleased to acknowledge the assistance given by Dr. S. L. Jones and Mr. C. Norman of Alcan International.

REFERENCES

1. Chang, C. D., Jacob, S. M., Silvestri, A. J., and Zahner, J. C., U.S. Patent 4,138,440 (1979).
2. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47,** 249 (1977).
3. Reed, M. G., Jaffe, J., U.S. Patent 3,798,177 (1974); 4,060,480 (1977).
4. Vaughan, D. E. W., Lussier, R. J., and Magee, J. S., U.S. Patent 4,176,090 (1979)
5. Lussier, R. J., Magee, J. S., and Vaughan, D. E. W., *in* "Proceedings, 7th Canadian Symposium on Catalysis" (S. E. Wanke and S. K. Chakrabarty, Eds.), p. 88. Chem. Inst. Canada, 1980.
6. Lahav, N., Shani, U., and Shabtai, J., *Clays Clay Miner.* **26,** 107 (1978).
7. Shabtai, J., Lazar, R., and Oblad, A. G., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 828. Elsevier, Amsterdam, 1981.
8. Occelli, M. L., and Tindwa, R. M., *Clays Clay Miner.* **31,** 22 (1983).
9. Occelli, M. L., *Ind. Eng. Chem. Prod. Res. Dev.* **22,** 553 (1983).
10. Gaaf, J., van Santen, R., Knoester, A., and van Wingerden, B., *J. Chem. Soc., Chem. Commun.*, 655 (1983).
11. Occelli, M. L., Parulekar, V. N., and Hightower, J. W., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. IV, p. 725. Verlag Chemie, Weinheim, 1984.
12. Shabtai, J., Massoth, F. E., Tokarz, M., Tsai, G. M., and McCauley, J., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. IV, p. 735. Verlag Chemie, Weinheim, 1984.
13. Kikuchi, E., Hamana, R., Nakano, M., Takehara, M., and Morita, Y., *J. Jpn. Pet. Inst.* **26,** 116 (1983).
14. Yamanaka, S., and Brindley, G. W., *Clays Clay Miner.* **27,** 119 (1979).
15. Burch, R., and Warburton, C. I., *J. Catal.* **97,** 503 (1986).
16. Meier, W. M., and Olson, D. M., *in* "Atlas of Zeolite Structure Types." International Zeolite Association, 1978.
17. Chen, N. Y., and Reagan, W. J., *J. Catal.* **59,** 123 (1979).
18. Balkrishnan, I., Rao, B. S., Hegde, S. O., Kotasthane, A. N., Kulkarni, S. B., and Ratnaswamy, P., *J. Mol. Catal.* **17,** 261 (1982).
19. Gives, E. N., Plank, C. J., and Rosinski, E. J., U.S. Patent 4,079,095 (1978).
20. Fraissard, J., "Catalysis by Zeolites," p. 343. "Elsevier, Amsterdam, 1980.