SiO$_2$ and Al$_2$O$_3$ as Oxidation Catalysts of Methanol

L. CAIRATI AND F. TRIFIRÒ[1]

Facoltà di Chimica Industriale, Viale Risorgimento 4, 40136 Bologna, Italy

Commercial silica and alumina were found to oxidize methanol to CO, methyl formate, CH$_2$O, and CO$_2$, in a fluidized bed reactor. The activity of SiO$_2$ was found to depend on the partial pressure of oxygen and could be markedly reduced either by decreasing the surface area or by adding Na$^+$ or Mg^{2+} ions. Methyl formate was obtained with SiO$_2$ as the main product with intermediate values of surface area and temperature. Silica and alumina gave a different range of oxidized products. The oxidation properties of SiO$_2$ and Al$_2$O$_3$ have been attributed to the formation of surface formates.

1. INTRODUCTION

SiO$_2$ and Al$_2$O$_3$ are well known both as acid–base catalysts and as supports for hydrogenation and oxidation reactions (*1*).

In previous papers (*2–4*) both SiO$_2$ and Al$_2$O$_3$ have been used as support for the Fe$_2$O$_3$–MoO$_3$ systems in the oxidation of methanol to formaldehyde. The oxidation of methanol is usually catalyzed by transition metal oxides (*5*) and it is also used as a model reaction to characterize solid solutions (*6, 7*) or interactions of oxides with supports (*8*).

In this work the catalytic properties of SiO$_2$ and Al$_2$O$_3$ have been investigated, under the same experimental conditions at which oxidation of methanol has been carried out with supported catalysts, that is to say, in air and in a fluidized bed reactor.

This was done with the aim of proving the role of the support itself in decreasing the selectivity in CH$_2$O in oxidation of methanol with supported catalysts.

Different surface areas of silica and Al$_2$O$_3$ and the effect of doping with Na$^+$ and Mg^{2+} ions have been investigated in this paper in order to find supports which are less active in the transformation of methanol into undesired by-products.

[1] To whom correspondence should be sent.

2. EXPERIMENTAL

Silica samples with different surface areas have been prepared by calcining microspheroidal silica (Grace 951) at 1200°C for different lengths of time. The purity of SiO$_2$ was 99.5% and the amount (wt% on dry basis) of other elements was: Al$_2$O$_3$, 0.15; Na$_2$O, 0.10; Fe, 0.03; CaO, 0.10. Commercial alumina Saint Gobain ($S = 120$ m^2/g) and Alcoa T-60 ($S = 1$ m^2/g) have been used. SiO$_2$[100] indicates SiO$_2$ with 100 m^2/g of surface area.

The oxidation of CH$_3$OH was carried out in two different reactors, a Pyrex reactor (i.d. = 28 mm) and a stainless-steel reactor (i.d. = 39 mm), both provided with a sinterized metal porous plate distributor (mean diameter of the holes 5 mm). The reaction conditions were: $H_0 = 35$ cm, $V = 12.2$ cm/sec, $p = 1$ atm in the case of the Pyrex reactor; $H_0 = 104$ cm, $V = 6$ cm/sec, $p = 1$ atm in the case of the stainless-steel reactor. The symbol $H_0 = $ the height of the bed. Fluidization was good near the grid, but slug flow regime was obtained on the top of the reactor; see Ref. (*4*). During the 60 h of investigation the catalysts were stable in activity and selectivity.

Nominal contact times were $\tau = 3$ sec in the Pyrex reactor and $\tau = 17$ sec in the stainless-steel reactor. The fluidizing gas

consisted of 5.5% methanol in air. Air is obtained from a compressed gas cylinder through a pressure regulator and metered on a rotameter and liquid methanol is supplied through a metering micropump. The two streams are mixed and heated for methanol evaporation up to the reactor.

The composition of gas from the reactor inlet and outlet has been analyzed in two gas chromatographs: a Perkin–Elmer model 154 with a molecular sieve 5-Å column (1 m long) at 50°C for O_2, N_2, and CO analysis and a Hewlett–Packard model 5700 A with a Porapack N column (1.8 m long) at 140°C for CO_2, CH_2O, H_2O, CH_3OH, methyl formate (MeFo), dimethyl ether (DME) analysis. The reactor temperature was measured by a thermocouple placed at the center of the catalytic bed.

3. RESULTS

In Figs. 1–4 the conversion of methanol and the yields of the different products obtained respectively with SiO_2[2], SiO_2[15], SiO_2[39], and SiO_2[100] at different temperatures are shown.

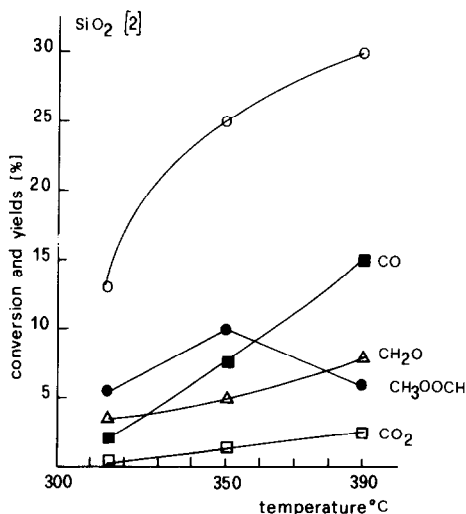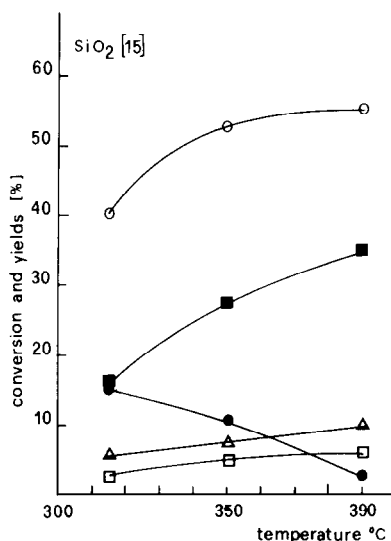In Fig. 5 the conversion of methanol and the yields of different products for

FIG. 2. Conversion and yields in oxidation of methanol with SiO_2[15] vs temperature of reaction. Symbols as in Fig. 1.

SiO_2[100] at 280°C as a function of oxygen partial pressure have been reported.

In Table 1 the yields of the different products for SiO_2[320] both pure and when doped with Na^+ and Mg^{2+}, for Al_2O_3[120], and for Al_2O_3[1] at 340°C have been reported.

FIG. 1. Conversion and yields in oxidation of methanol with SiO_2[2] vs temperature of reaction. O = conversion; △ = CH_2O yield; ● = methyl formate yield; ■ = CO yield; □ = CO_2 yield.
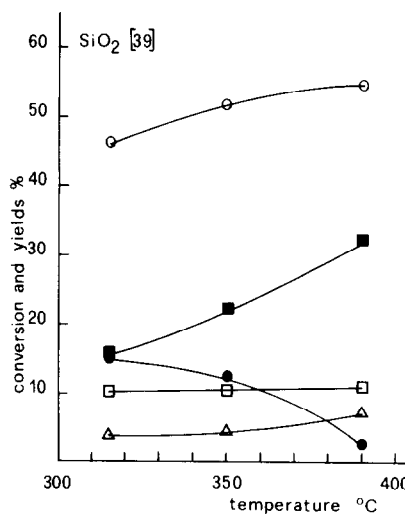
FIG. 3. Conversion and yields in oxidation of methanol with SiO_2[39] vs temperature of reaction. Symbols as in Fig. 1.
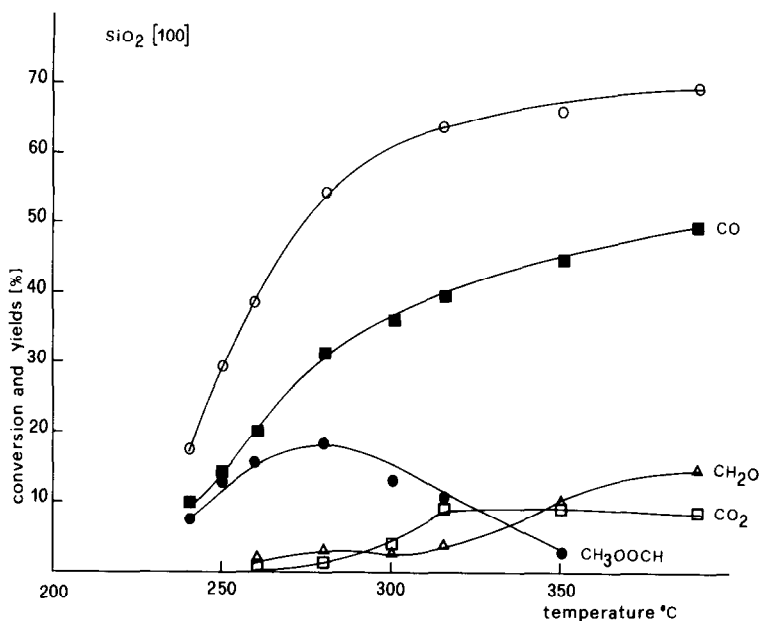
FIG. 4. Conversion and yields in oxidation of methanol with $SiO_2[100]$ vs temperature of reaction. Symbols as in Fig. 1.

All these last data have been obtained with the stainless-steel reactor with a contact time of 17 sec. In the same table the data of $SiO_2[100]$ both pure and doped with Na^+ obtained at 340°C with the Pyrex reactor with a contact time of 3 sec have been reported.

FIG. 5. Conversion and yields in oxidation of methanol with $SiO_2[100]$ at 280°C vs oxygen partial pressure. Symbols as in Fig. 1.

4. DISCUSSION

The results obtained have shown that even not generally considered oxidation catalysts such as SiO_2 and Al_2O_3 can be active in oxidation reactions of methanol yielding a large spectrum of products.

Factors which determine their oxidation properties are the following: (i) the surface area of the catalyst, (ii) the concentration of oxygen in the gas phase, (iii) the presence or the absence of Na^+ and Mg^{2+} ions at the surface. With the aim of proving the role of the surface area of SiO_2 in determining its oxidative properties, the conversion of methanol and the yields of products at 315°C have been plotted in Fig. 6 as a function of its surface area.

The most interesting product is methyl formate which can be obtained as the main product together with CO at an intermediate value of surface area and temperature. A maximum in fact was observed in yield of methyl formate either with temperature or
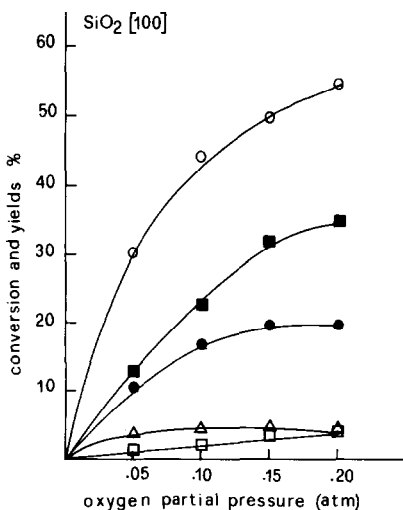
TABLE 1

Activity and Selectivity Data in the Oxidation of Methanol in a Fluidized Bed Reactor

	CH$_3$OH conversion (%)	Yield (%)				
		CH$_2$O	MeFo[a]	DME[b]	CO	CO$_2$
SiO$_2$[320]	70	8	5	0	32	22
SiO$_2$[320] + 1.6% Na$_2$O[c]	32	0	0	24	4	3
SiO$_2$[320] + 1.6% MgO	40	0	0	0	31	6
SiO$_2$[320] + 5.0% MgO	39	0	0	16	20	2
SiO$_2$[100][d]	70	9	4	0	42	10
SiO$_2$[100][d] + 0.5% Na$_2$O[c]	6	1	0	0	4	2
Al$_2$O$_3$[120]	89	0	0	6	79	10
Al$_2$O$_3$[1]	30	3	0	2	6	18

Note. Experimental conditions: height of the bed, $H_0 = 104$ cm; linear velocity, $V = 6$ cm/sec; methanol concentration, 5.5%; $T = 340°C$.

[a] MeFo = methyl formate.
[b] DME = dimethyl ether.
[c] The surface coverage of Na$_2$O was less than 30%.
[d] With Pyrex reactor $\tau = 3$ sec.

surface area. The decrease in yield of methyl formate, increasing surface area, occurs with the formation of a higher yield of CO. The decrease in methyl formate yield with the increase in temperature occurs with a sharp increase of both CO and CH$_2$O.

In this case the formation of CO and CH$_2$O is due to the decomposition of methyl formate as only a slight increase of conversion occurs with temperature.

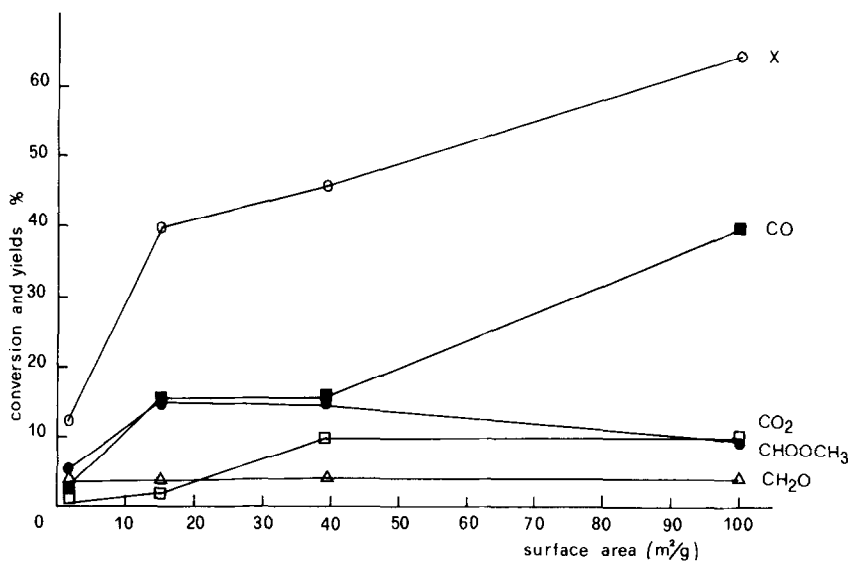It is assumed that the formation of methyl formate occurs through the esterification of previously formed HCOOH.

FIG. 6. Conversion and yields in oxidation of methanol at 315°C with SiO$_2$ of different surface area. Symbols as in Fig. 1.

Traces of HCOOH have always been observed especially at low temperatures. The esterification of HCOOH saves it from further decomposition.

The yield of methyl formate depends on oxygen concentration as can be deduced from Fig. 5.

The addition of Na$^+$ and Mg^{2+} destroys at first the centers which are responsible for the formation of methyl formate, of CH$_2$O, and of CO$_2$. With higher amounts of magnesium and sodium the centers responsible for formation of CO are also destroyed and dimethyl ether has been observed in the products.

A second product of partial oxidation was CH$_2$O. The yield of CH$_2$O does not depend either on surface area of silica or on partial pressure of oxygen.

In the temperature range investigated a continuous increase in CH$_2$O yield was observed for all values of surface area. CH$_2$O seems to form from the decomposition of methyl formate, although it is not possible to exclude an independent route.

CO is the main product, especially at high temperature. The formation of CO depends on partial pressure of oxygen and it seems to derive in great part from the decomposition of methyl formate. The effect of Mg^{2+} (shown in Table 1) revealed that a specific center exists at the SiO$_2$ surface, responsible for the formation of CO.

The formation of CO$_2$ which depends on partial pressure of oxygen and which is present only in relatively large amounts with SiO$_2$ with high surface area does not seem to be related to the successive oxidation of methyl formate or CH$_2$O. In fact at the temperature at which methyl formate decreases CO$_2$ does not increase.

Few results have been reported on Al$_2$O$_3$; however, it is possible to deduce that it is active in oxidation and the spectrum of products is slightly different from the SiO$_2$ one.

From all the data reported here it is possible to conclude that the slightly acidic oxides such as SiO$_2$ and Al$_2$O$_3$ are able to oxidize methanol in a fluidized bed reactor.

These oxidation properties can be summarized as:

(i) oxygen insertion properties: formation of CO$_2$ and HCOOH (methyl formate),

(ii) oxidative dehydrogenation: formation of CO and CH$_2$O and decomposition of methyl formate.

All these properties depend on partial pressure of oxygen and can be strongly decreased by adsorption of Na$^+$ and Mg^{2+} ions.

In order to discuss the nature of active sites, attention will only be given to the formation of methyl formate. CO$_2$ and CH$_2$O have been found only in small amounts and CO seems to be formed from the decomposition of methyl formate.

The oxidation of methanol on transition metal oxides yields CO$_2$ (5) and that on molybdates yields CH$_2$O and CO (3).

SiO$_2$ and Al$_2$O$_3$ behave differently from the previous two classes of catalysts. In fact formic acid seems to be the key product in the oxidation of CH$_3$OH on SiO$_2$ as catalyst (and very probably also on Al$_2$O$_3$).

Formic acid is esterified at low temperature and/or with low-surface-area SiO$_2$ to methyl formate or dehydrated at high temperature and/or with high-surface-area SiO$_2$ to CO.

Formation of Si–O–O–O–Si groups was suggested to occur in the adsorption of oxygen on quartz surface (9, 10). These peroxy compounds are able (10) to oxidize CO to CO$_2$.

As CO$_2$ has always been present in small amount except on SiO$_2$[320] we conclude that these peroxides are not the active sites for the oxidation of CH$_3$OH to CHOOH.

Burwell and co-workers (11, 12) attributed the catalytic activity of SiO$_2$ to traces of impurity. We cannot exclude that traces of Al(III) are responsible for the acidity of SiO$_2$. We do not believe traces of Fe(III) are the oxidation sites of SiO$_2$, on the basis of the small amount of CO$_2$ formed and the

poisoning effect of sodium and magnesium addition.

Formation of formates was observed in the adsorption of methanol on Al_2O_3 (13). These species to our knowledge were not observed in the adsorption of methanol on SiO_2. However, surface benzoates were found in the adsorption of benzaldehyde and benzilic alcohol on SiO_2 (14).

We attribute the oxidation of methanol to the formation of surface formates which can be esterified to methyl formate or dehydrated to CO.

Armor et al. (15, 16) found also that SiO_2 is active in ammoximation of cyclohexanone and attributed to the formation of $Si-NH_2$ and $Si-NH-Si$ groups a key role in the whole oxidation process.

We think also the oxidation of methanol occurs through the elimination of proton from surface methoxy group by adjacent oxygen ions and therefore the catalytic activity of SiO_2 and Al_2O_3 in oxidation reaction is due to their weak acidity.

Very probably gaseous oxygen is involved later in repristinating the oxidation state of the surface.

ACKNOWLEDGMENTS

REFERENCES

1. Germain, J. F., in "Catalytic Conversion of Hydrocarbons." Academic Press, New York, 1969.
2. Cairati, L., Carbucicchio, M., Ruggeri, O., and Trifirò, F., in "Preparation of Catalysts II" (I. B. Delmon, P. Grange, P. Jacobson, and G. Poncelet, Eds.), p. 279. Elsevier, Amsterdam, 1979.
3. Carbucicchio, M., and Trifirò, F., J. Catal. 62, 13 (1980).
4. Cairati, L., Di Fiore, L., Forzatti, P., Pasquon, I., and Trifirò, F., Ind. Eng. Chem. Process Des. Dev. 19, 561 (1980).
5. Trifirò, F., and Pasquon, I., J. Catal. 12, 412 (1968).
6. Awe, A. A., Miliades, G., and Vickerman, C., J. Catal. 62, 202 (1980).
7. Ai, M., J. Catal. 60, 306 (1979).
8. Roozenboon, F., Cordinglers, P. D., and Gillings, P. J., J. Catal. 68, 464 (1981).
9. Bystrikov, A. V., Streletskii, A. N., and Butyagin, P. Yu., Kinet. Katal. 21, 1148 (1980).
10. Kolbanev, V., Berestetskaya, V., and Butyagin, P. Yu., Kinet. Katal. 21, 1154 (1980).
11. Burwell, R. L., Jr., Chem. Tech., 370 (June 1974).
12. West, P. B., Haller, G. H., and Burwell, R. L., J. Catal. 29, 486 (1973).
13. Greenler, R. G., J. Chem. Phys. 37, 2094 (1962).
14. Deflin, M., Eltantowy, I. M., and Baverez, M., J. Catal. 54, 345 (1978).
15. Armor, J. N., Carlson, F. J., Saled, S., Conner, W. C., Laverich, A., De Rites, B., and Gates, W., J. Catal. 70, 84 (1981).
16. Armor, J. N., and Zambri, P. M., J. Catal. 73, 57 (1982).