The low-temperature conversion of methyl formate on zirconium oxide

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Zirconium oxide samples prepared by a variety of methods were found to have surface areas from 7 to 226 m^2/g and relative amounts of tetragonal to (tetragonal + monoclinic) phases from 0 to 100%. Methyl formate is converted to carbon monoxide and methanol on these samples at temperatures of 220–265°C. All catalyst samples examined are stable at these temperatures for times-on-stream up to 3 h. Although the conversion varies with the relative amounts of tetragonal phase present and decreases with increase in the calcination temperature, a clear dependence on surface area is also observed. The conversion of methyl formate is found to be first order with activation energies of 80 (±10) kJ/mol. The data can be fitted to a Langmuir–Hinshelwood equation.

Keywords: Zirconium oxide; methyl formate conversion; low temperature conversion

1. Introduction

Interest in methyl formate (MF) has increased during the last decade, at least in part due to the recent focus on energy-efficient processes [1,2]. Much of the impetus for the research activity is related to the potentialities of the production of methanol from synthesis gas via methyl formate [3–8]. Thus there are two aspects of catalytic interest, namely those related to the formation of MF on one hand and those concerned with its decomposition and hydrogenolysis to methanol. The formation of MF from methanol has been studied over a variety of catalysts [9–11]. The mechanism of the formation of MF on Cu/ZnO catalysts has recently been investigated through the use of isotopic labelling [12]. The adsorption of MF on copper/SiO_2 catalysts has been examined through the use of infrared spectroscopy [13]. The hydrogenolysis of MF has been studied by a number of workers [3–8] and most recently the decomposition of MF has been studied on magnesium oxide doped with sodium hydroxide [14]. In the latter work the authors concluded that strong basic centers are the active sites.

Zirconium oxide is a particularly interesting oxide for a number of reasons. It is claimed to be the only metal oxide catalyst whose surface possesses four chemical attributes: acidic, basic, oxidizing and reducing properties [15,16]. Zirconia exhibits polymorphism, that is it is capable of existing in at least three different crystalline forms, monoclinic, tetragonal and cubic, although another high pressure orthorhombic form has recently been reported [17]. The monoclinic phase converts to the tetragonal form at about 1150°C while the reverse transformation occurs at about 950°C on cooling.

Recent work in this laboratory has shown that methane can be converted to ethane on zirconium oxide at temperatures as low as 530°C, although the percent conversion, not surprisingly, is low [18]. Since various workers have suggested that methane activation occurs on basic sites it appeared worthwhile and interesting to study the decomposition of MF on zirconium oxide and to evaluate the dependence of this latter process on phase composition. Although there has been considerable interest in zirconium oxide as a catalyst in recent years much of the work has centered on the use of this solid as a support. However, Davis and coworkers have studied a wide variety of aspects of the properties and applications of ZrO_2 including preparative and stabilization techniques for the several phases [16,19]. Investigations by other workers have been concerned with infrared studies of ethane and ethene adsorption [20,21] applications in the oxidative dimerization of methane [22] and a variety of other catalytic processes [23–25].

2. Experimental

Zirconium hydroxide samples were precipitated from a zirconium tetrachloride (Aldrich 99.9$^+$%) solution (0.3 mol/ℓ) by the addition of a calculated amount of ammonium hydroxide solution to produce a gelatinous solution which had the final pH (usually 10.4), following the procedures proposed by Davis and coworkers [16]. Some samples were aged in the mother liquor at the final pH with stirring. The resultant precipitate was collected by filtration. The collected zirconium hydrous gel was washed with distilled water repeatedly. The white gel thus obtained was dried in air at 120°C overnight and calcined in static air at 500°C for 4 h unless otherwise stated. The preparation procedures and physical properties of the zirconium oxide catalysts are summarized in table 1.

Catalysts nos. 330-300, 330-400, 330-500, 330-600 and 330-700 were obtained by calcination of zirconium hydroxide no. 330 for 4 h at 300, 400, 500, 600 and 700°C, respectively. Their physical properties are also shown in table 1. ZrO_2-Ald is a monoclinic ZrO_2(99.99$^+$%) purchased from Aldrich.

Powder X-ray diffraction patterns were recorded on a Siemens model D500 diffractometer using nickel-filtered Cu Kα radiation. Patterns were recorded over the range 2θ = 5–70°. The catalyst was a mixture of monoclinic and tetragonal

Table 1
Preparation and physical properties of various ZrO_2

Catalyst	Final pH (F-time[a])	Aging (h)	Calcination temp.(°C)	BET (m^2/g)	%T
KS275	10.4(16)	–	500	87.3	85
KS306	6.0(0.3)	–	500	60.6	6
KS307	10.4(8)	5	500	80.9	64
KS313	10.4(6.5)	–	500	84.4	19
KS314	10.4(11)	–	500	64.9	44
KS316	10.4(5)	–	500	61.0	17
KS318	10.4(8)	24	500	77.1	100
KS321	10.4(3.5)	12	500	72.4	92
KS322	3.5(0.1)	–	500	59.3	54
KS329	10.4(0.5)	–	500	45.8	13
ZrO_2-Ald	–	–	–	6.9	0
KS330-300	10.4(6)	–	300	226.4	am.[b]
KS330-400	10.4(6)	–	400	97.8	47
KS330-500	10.4(6)	–	500	60.9	19
KS330-600	10.4(6)	–	600	45.4	19
KS330-700	10.4(6)	–	700	17.0	18

[a] Time to attain the final pH (h).
[b] am: amorphous.

phases. The molar % of tetragonal phase (%T) was calculated from the ratio of the peak intensities [25]:

$$\frac{(1,1,1)_T}{[1.6 \times (1,1,-1)_M + (1,1,1)_T]},$$

where T and M denote tetragonal and monoclinic phases, respectively. The BET surface areas of the zirconium oxides were measured by nitrogen adsorption at −196°C.

The activities of the catalysts were determined using a continuous flow microcatalytic reactor mounted horizontally and operated at atmospheric pressure. The reactor consisted of a 6 mm i.d. and 8 mm length quartz tube sealed to 4 mm i.d. quartz tubes on both ends. A measured amount of catalyst (usually 0.2 g) was placed in the 6 mm portion of the quartz tube with plugs of quartz wool at both ends. The temperature was measured by a thermocouple placed in contact with the outside wall of the reactor. Methyl formate (MF) was introduced into the reactor by passing helium gas through two saturators connected in series at ice-water temperature. The partial pressure of MF at ice-water temperature was 196 Torr. The total flow rate was 30 ml/min unless otherwise stated. The catalyst was heated at 250°C for 0.5 h in a 25 ml/min O_2 flow just before the reaction. All sections of the reactor system through which MF flowed were heated to temperatures of at least

150°C. The reactant and products were analyzed on an on-line HP5890A gas chromatograph equipped with a TC detector and helium carrier gas. HayeSep DIP (5.4 m × 3.1 mm, programmed 50–200°C) was used to analyze H_2, CO, CO_2, H_2O, CH_3OH, DME (dimethyl ether) and MF. The conversion of MF was calculated from the ratio of non-MF carbon-containing molecules to total carbon-containing molecules in the exit gas on a carbon-atom base. The selectivity of each product was calculated from the conversion of MF to each product on a carbon-atom base.

Methyl formate purchased from Aldrich (99^+%) was used without further purification.

3. Results

The main products were carbon monoxide and methanol. The formation of hydrogen was not observed. The molar ratio of carbon monoxide to methanol was 1.1–1.3 (usually around 1.2). A small amount of DME (dimethyl ether) was detected in the exit gas over most of the catalysts (0–2% of methanol was converted to DME). Small quantities of carbon dioxide (ca. 0–1% selectivity) were produced probably due to the reaction of carbon monoxide with zirconium oxides and/or contaminated oxygen gas. Supplementary experiments showed that under the conditions employed in the present work, the conversion of the product methanol is negligible.

The carbon material balance was 100 ± 5%. The colour of the catalyst changed from white to light yellow or light brown after the reaction, suggesting that carbonaceous material were deposited over the catalyst surface. The carbonaceous species could be removed by heating at 250°C for 0.5 h in an O_2 stream.

The catalytic performances of various ZrO_2 catalysts with time-on-stream at 250°C are summarized in fig. 1. It is obvious that the catalytic activity of ZrO_2 was almost constant during 3 h on-stream over all catalysts. Fig. 2 illustrates the dependence of the conversion of MF on phase composition. The fraction of the tetragonal phase (%T) and BET surface area remained almost constant during 3 h on-stream.

Various ZrO_2 were prepared by changing the calcination temperature of the zirconium hydroxide gel and their catalytic activities were tested. The results are summarized in fig. 3. The conversion of MF slightly increased at first, passed through a maximum at the calcination temperature of 400°C and then decreased with the increase in the calcination temperature. At the same time the conversion of MF normalized by BET surface area first increased with calcination temperature, reached a maximum at 500°C and then decreased with increasing calcination temperature. These facts suggested that the surface property, probably surface hydroxyl groups, strongly related to the catalytic activity of zirconium oxide in the decomposition reaction of MF.

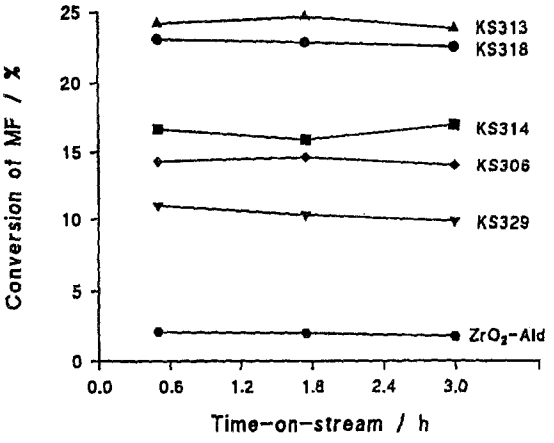

Fig. 1. Conversion of methyl formate over ZrO_2. Catalyst at various times-on-stream (0.2 g ZrO_2; feed 30 ml/min, MF 196 Torr, He balance, reaction temperature 250°C). See table 1 for phases present.

Increases in resistance time (W/F) produced increases in conversion of MF, as expected. The data yield good fits to first order rate equation plots for various temperatures from 220 to 265°C (fig. 4). Arrhenius plots for the same data produced good linear correlations (fig. 5). Activation energies for KS318, KS313 and ZrO_2-Ald were calculated as 69, 93 and 89 kJ/mol, respectively.

Increases in the partial pressure of MF produced decrease in the percent conversion of MF, although the quantity of MF converted increases. Good linear correlations between 1/(MF converted) and $1/P$ were obtained (fig. 6).

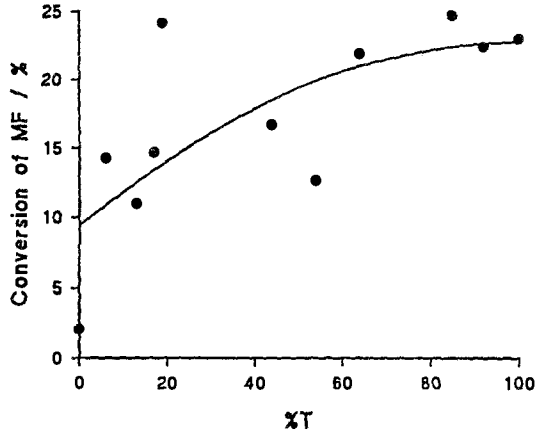

Fig. 2. Dependence of conversion of methyl formate on phase composition.

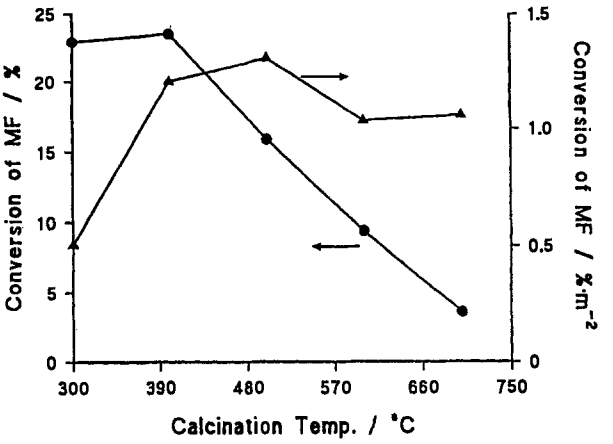

Fig. 3. The effect of calcination temperature on conversion of methyl formate (reaction conditions as in fig. 1 except 0.5 h on-stream and KS330 catalyst).

4. Discussion

Although the data provided in fig. 2 suggests at least an approximate dependence of the conversion of MF on the phase composition, the conversion appears to be more directly related to surface area (fig. 7). While there is, of course, a dependence of the surface area on the phase composition there appears to be no unambiguous evidence to suggest that either phase, monoclinic or tetragonal, is superior in catalytic activity in the MF process. Thus the process must be considered to be structure insensitive, at least where ZrO_2 is a catalyst and under the conditions employed in the present work.

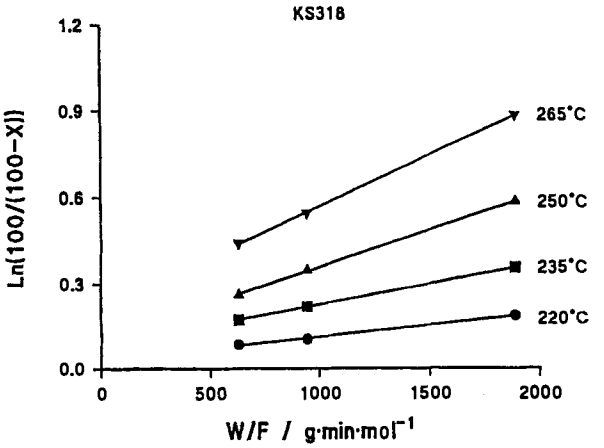

Fig. 4. First order plots for conversion of methyl formate on tetragonal ZrO_2.

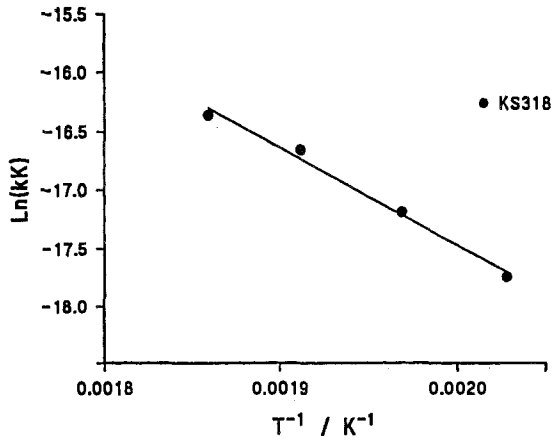

Fig. 5. Arrhenius plot for tetragonal ZrO_2 sample.

The reduction in conversion of MF with the increasing calcination temperature can be attributed both to a reduction in surface area as well as a loss in the number of active sites. In view of the findings of Ma et al. [14] these are most probably hydroxyl groups.

The first order rate dependence is not unexpected for a decomposition process that, on the basis of products formed, seems unlikely to require more than one molecule for each elementary step. Although there is evidence for a Langmuir–Hinshelwood mechanism, it is well known that this should not be overemphasized. However, a mechanism in which the MF adsorbs and decomposes on the surface seems not unreasonable. Calculated activation energies varied from 68.8 kJ/mol for the tetragonal ZrO_2 to 89.2 kJ/mol for the monoclinic. Although it is

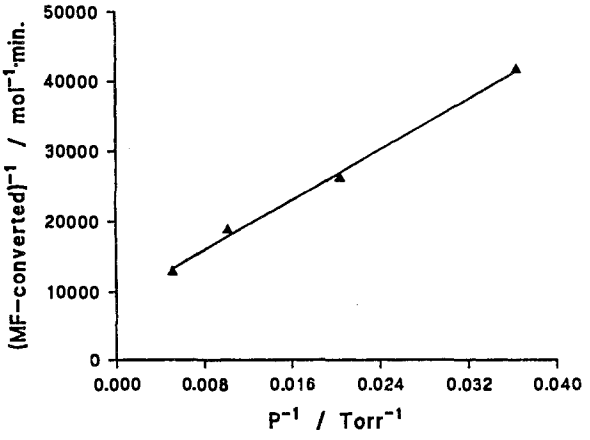

Fig. 6. Langmuir–Hinshelwood plot for ZrO_2 sample containing 19% tetragonal phase.

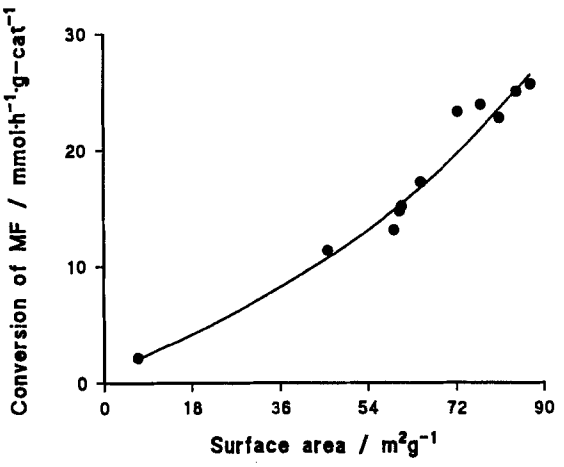

Fig. 7. Dependence of the conversion on surface area of zirconia samples.

tempting to suggest that this reflects a difference in the catalytic properties of the two phases of ZrO_2 it appears more prudent to relate such differences to experimental error.

Finally, it is interesting to compare our results on ZrO_2 with those of Ma et al. [14] on magnesium oxide doped with sodium hydroxide. While the highest conversion obtained with ZrO_2 was approximately 25%, values of approximately 40% were obtained with the doped magnesium oxide catalyst under the same reaction conditions. However, with the latter catalyst a rapid deactivation occurred in the first two hours while ZrO_2 showed little or no deactivation during this time. In the case of ZrO_2 an insignificant loss in surface area occurs during reaction at 250°C and the stability of the catalyst appears to be attributable not only to this property but also to the apparent invariance of the surface sites under the operating conditions.

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