Catalysis Letters 13 (1992) 283–288

Mechanism for the formation of carbon dioxide in the catalytic oxidation of carbon monoxide and methane on silica

Yasuyuki Matsumura [1], Keiji Hashimoto [2] and John B. Moffat [1,*]

[1] Department of Chemistry, University of Waterloo, Waterloo Ontario, Canada, N2L 3G1
[2] Osaka Municipal Technical Research Institute, Joto-ku, Osaka 536, Japan

Received 9 December 1991; accepted 28 January 1992

The oxidation of carbon monoxide to carbon dioxide is shown to be catalyzed at 850 K or above over almost all lattice oxygen atoms on the surface of silica prepared by the sol-gel method from ethyl orthosilicate under conditions which yield high selectivity to carbon dioxide in the oxidation of methane.

Keywords: Silica; oxidation; methane; carbon monoxide; carbon dioxide; labelled reaction

1. Introduction

The possibility of enhancing the utilization of methane through processes such as the oxidative coupling and/or the partial oxidation of methane continues to occupy the attention of many scientists worldwide [1]. Unfortunately, selectivities to the desired products are generally less than are necessary for economical operation of these processes, at least in part as a consequence of the generation of quantities of carbon dioxide. While there have been considerable efforts to understand the mechanism by which carbon dioxide is formed agreement among the various workers has not been achieved. In the present work the oxidation of carbon monoxide to carbon dioxide is shown to be catalyzed at 850 K or above over almost all lattice oxygen atoms on the surface of silica prepared by the sol-gel method from ethyl orthosilicate under conditions which yield high selectivity to carbon dioxide in the oxidation of methane.

Silica has been employed as a support in studies of the oxidation of methane [2–21]. Work in this laboratory and elsewhere [3,4,22–24] has shown that silica itself is capable of catalyzing the oxidation of methane, although the products

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[*] To whom correspondence should be addressed.

retained depend on the oxidant used. It has been shown that the product distribution from the oxidation of methane varies with the sample of silica, although the samples are apparently similar in composition [4,22–24]. It has been suggested that the surface area of silica is an important factor in the catalytic activity of the silica [22]. Work from one of our laboratories has shown that silica prepared by the sol-gel method yields a high selectivity to carbon dioxide in the oxidation of methane, as compared with that prepared from inorganic compounds, although the surface areas of the products prepared by these two methods were little different.

To provide further information on the mechanism by which carbon dioxide is formed, the reaction between carbon monoxide and oxygen labelled with ^{18}O has been studied on silica prepared by sol-gel method. If the lattice oxygen is activated in the reaction process, almost all of the lattice oxygen atoms on the silica surface appear to be reactive to carbon monoxide.

2. Experimental

Ethyl orthosilicate (Kanto Chemical Corp. [G.R. Grade]) was hydrolysed to silica gel in a 5M nitric acid solution. The hydrogel obtained was dried at ca. 400 K in air, washed with water and heated at 720 K in air for 5 h. Analysis by atomic absorption spectroscopy showed that this sample (SiO_2–O) has no observable impurities. For comparison purposes, a silica sample prepared from inorganic compounds (Cariact-15) was obtained from Fuji-Davison Chemical Ltd. The BET surface areas of these samples in powdered form was 245.1 and 177.9 $m^2\ g^{-1}$, respectively.

The oxidation of carbon monoxide was carried out in a static reactor of dead volume ca. 0.1 dm^3 equipped with a Baratron pressure gauge. The catalysts were held in a quartz tube of 6 mm inner diameter. The reactant gas contained carbon monoxide and oxygen in a molar ratio of 2/1, respectively. Tests showed that the reaction gas was well dispersed in the reactor below a pressure of 100 Pa. The reaction products were analyzed with a mass spectrometer (ULVAC MSQ-150A).

Methane oxidation was performed in a conventional quartz flow reactor (8 mm i.d.) Reactants were diluted with helium gas and the total flow rate was 0.015 $dm^3\ min^{-1}$.

3. Results and discussion

SiO_2-O was found to catalyze the oxidation of carbon monoxide at temperatures as low as 850 K (fig. 1) while Cariact-15 showed only a small activity for this reaction. The reaction rate was initially slow but subsequently increased

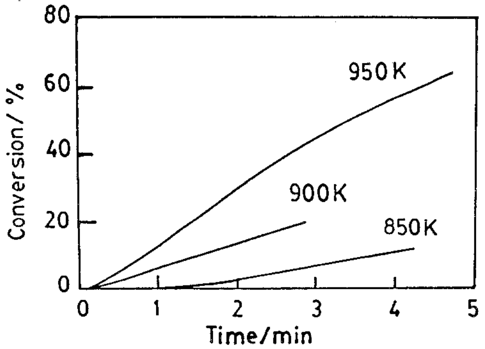

Fig. 1. Carbon monoxide to carbon dioxide over silica prepared by the sol-gel method. Catalyst; SiO_2–O, 0.0052 g: Initial pressure of carbon monoxide, 50 Pa; oxygen, 25 Pa. Prior to the runs shown here, the catalysts were activated by more than 6 runs at 950 K.

abruptly, possibly indicating an activation process in the reaction. Experiments in which the initial pressure of the reactants was varied confirmed that, subsequent to the rate acceleration period of time, the rate is dependent upon the pressure. The apparent activation energy was calculated as 90 kJ mol^{-1} from Arrhenius plots for the rate at 10% conversion. Although a liquid nitrogen trap was usually employed to remove carbon dioxide from the reaction gas, no significant change was observed in the absence of this trap. The reaction proceeds stoichiometrically and does not occur in the absence of oxygen gas at 950 K ($P_{CO} = 50$ Pa).

In contrast to the aforementioned results, the catalytic activity of Cariact-15 in the oxidation of methane is very high compared with that of SiO_2–O while SiO_2–O showed noticeably higher and lower selectivity to carbon dioxide and carbon monoxide, respectively, than Cariact-15 (table 1). This suggests that there are active sites in SiO_2–O which selectively catalyze the oxidation of carbon monoxide.

To obtain further information on the nature of these sites, the oxidation of carbon monoxide on SiO_2–O was studied with $^{18}O_2$ contained in the reactant mixture. The catalyst was preheated *in vacuo* (ca. 10^{-3} Pa) for 0.5 h at 950 K.

Table 1
Activity and selectivity of silica for methane oxidation [a]

Catalyst	Reaction temp./K	Conversion/%		Selectivity/%				
		CH_4	O_2	C_2H_6	C_2H_4	H_2CO	CO	CO_2
SiO_2-O	1020	2.7	19.0	20.2	14.4	0.3	30.1	34.2
Cariact-15	1020	14.1	99.2	4.3	3.4	6.2	69.2	16.1
Cariact-15	920	5.1	78.4	0.4	0.0	0.2	82.7	15.8

[a] Partial pressure of methane, 28.7 kPa; oxygen, 4.1 kPa. Catalyst (0.50 g) was preheated under oxygen stream at 1020 K for 1 h.

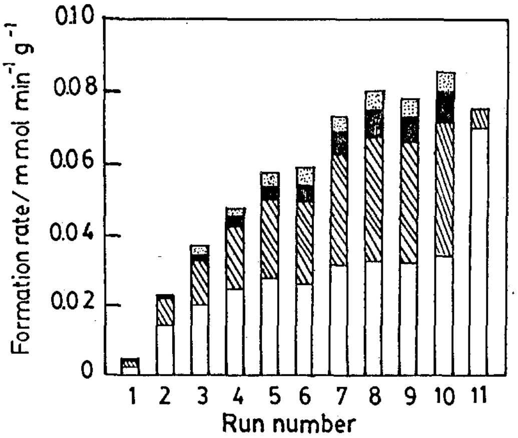

Fig. 2. Formation rates for products of the reaction between CO and $^{18}O_2$ over silica prepared by the sol-gel method. Catalyst; SiO_2–O, 0.0047 g: Initial pressure; carbon monoxide, 50 Pa; oxygen, 25 Pa: Reaction temperature 950 K. The rates were determined by division of products yield by period of the reaction; each run was stopped at conversion below 60%. Open bar, $C^{16}O_2$; hatched bar, $C^{16}O^{18}O$; solid bar $C^{18}O_2$; dotted bar, $C^{18}O$. Run 11 was carried out with $^{16}O_2$ instead of $^{18}O_2$.

The reaction was repeated on the same aliquot of catalyst after evacuation to 10^{-3} Pa for 0.2 h at 950 K after each reaction. The internal pressure was less than 0.1 Pa when the reaction system was isolated before the reaction, suggesting that the amount of adsorbed species on the catalyst surface is small and the number of ^{16}O included in these residual species is negligible. The rate of production of carbon dioxide in the initial experiment was found to be quite low (fig. 2) but increases with successive experiments up to a run number of 8. A small amount of hydrogen was detected in experiments 1 and 2 while SiO_2–O evacuated for 5 h at 950 K exhibited significantly higher activity in the initial experiment. These results suggest that the removal of surface water is, at least in part, responsible for the increase in activity. It is important to note that a considerable quantity of $C^{16}O_2$ was formed in the reaction. The total amount through runs 1 to 10 is 1.0 mmol g^{-1}. Since the total amount of $C^{18}O_2$ and $C^{18}O$ is 0.3 mmol g^{-1} and is small, most of the oxygen in $C^{16}O_2$ evidently originates from the lattice oxygen of SiO_2–O. The number of oxygen atoms on the surface of SiO_2 is estimated as 6 mmol g^{-1} based on its surface area and the density of silica. Thus approximately 12% of the lattice ^{16}O atoms on the surface are consumed in the reaction. With the last run (in which the reactant gas did not contain $^{18}O_2$), 8% of the carbon dioxide produced was $C^{16}O^{18}O$. This strongly suggests that lattice oxygen on the surface of SiO_2–O was replaced with ^{18}O. Since no formation of $^{16}O^{18}O$ or $^{16}O_2$ was observed in the previous runs, it appears that the replacement is not the result of exchange between the lattice oxygen and gas phase oxygen but rather occurs during the oxidation of carbon monoxide. As can be seen in the early runs, approximately one half of the carbon dioxide produced in $C^{16}O_2$. Thus it is estimated that 15% of the lattice oxygen atoms which can react with carbon monoxide are replaced with ^{18}O in the catalyst of the last run, and the number is approximately identical with the number of lattice ^{16}O consumed as calculated above.

It thus appears that almost all the lattice oxygen atoms on the surface of SiO_2–O participate in the oxidation process. Since these lattices oxygen atoms are generally considered to be inactive, an activation process must occur in the reaction. Production of $C^{18}O$ without the formation of $^{16}O^{18}O$ or $^{16}O_2$ was observed in runs 1 to 10 but no exchange between lattice ^{18}O and carbon monoxide occurred in the last run. Hence, the oxygen atom in carbon monoxide is not exchanged with that in either O_2 or the surface of silica, but probably with the surface atomic oxygen species such as O^- formed during adsorption, which readily reacts with carbon monoxide [25,26].

The formation of the adsorption species accounts well for the product distribution as follows. Assuming that the atomic oxygen species is O^-, an electron must remain on the surface of silica after the reaction between O^- and carbon monoxide to form carbon dioxide. If a Si–O^-–Si group is formed, the lattice oxygen will be reactive. Hence the reactions:

$$CO + O^- + Si\text{–}O\text{–}Si \rightarrow CO_2 + Si\text{–}O^-\text{–}Si \qquad (1)$$

$$CO + O_2 + Si\text{–}O^-\text{–}Si \rightarrow Si\text{–}OCO + O_2^-\text{–}Si \qquad (2)$$

$$Si\text{–}OCO + O_2^-\text{–}Si \rightarrow CO_2 + O^- + Si\text{–}O\text{–}Si \qquad (3)$$

would be expected to occur. In these reactions, one molecule of carbon monoxide reacts with a lattice oxygen and another reacts with oxygen originating from molecule oxygen. However this mechanism does not account for the source of the initial O^-. It is possible that special sites for the generation of O^- may be present in SiO_2–O. Since silica prepared by the sol-gel method contains Si–O–O–Si groups it seems reasonable to suggest that these are involved in the initial activation process [27,28].

Acknowledgement

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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