

Vanadium Oxide Monolayer Catalysts

The Vapor-Phase Oxidation of Methanol

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Received July 14, 1980

The oxidation of methanol over vanadium oxide, unsupported and applied as a monolayer on γ - Al_2O_3 , CeO_2 , TiO_2 , and ZrO_2 , was studied between 100 and 400°C in a continuous-flow reactor. At temperatures from 150 to about 250°C two main reactions take place, (a) dehydration of methanol to dimethyl ether and (b) partial oxidation to formaldehyde. A very slight direct oxidation to CO_2 proceeds simultaneously. At higher temperatures two further reactions take place, i.e., (c) consecutive oxidation of the ether and/or formaldehyde to CO and (d) consecutive oxidation of CO to CO_2 . Selectivity to formaldehyde increased with decreasing reducibility of the catalyst, which in turn was a function of the catalyst-support interactions. Since the reducibility of V(V) has been shown to be related to the charge/radius ratio of the cation of the carrier, the selectivity to formaldehyde is also determined by this ratio.

INTRODUCTION

The selective oxidation of methanol to formaldehyde has been studied by many authors (1-21), mainly because of its importance in the industrial production of formaldehyde (U.S. production in 1977: 2.8×10^6 tons). (1). The process was at first based on a silver oxide catalyst, but this was later replaced by MoO_3 - $\text{Fe}_2(\text{MoO}_4)_3$ which had high selectivity to formaldehyde (2). The present status of research on the mixed Fe-Mo catalyst has been reviewed by Pernicone (3).

As a sequel to the study of the oxidation activity of vanadium oxide monolayer catalysts (22-25) the activity and selectivity of these catalysts for the methanol oxidation have been studied. This paper deals with the catalytic behavior towards methanol oxidation on vanadium oxide, unsupported and supported as a monolayer (or monomolecular dispersion) on γ - Al_2O_3 , CeO_2 , TiO_2 , and ZrO_2 . In particular the possible

influence of the carrier oxides on the properties of the monolayer was investigated.

EXPERIMENTAL

Materials. Unsupported V_2O_5 was prepared from NH_4VO_3 (Merck, analytical grade) by thermal decomposition at 600 K for 2 h in a stream of air. The supports, γ - Al_2O_3 , CeO_2 , TiO_2 , and ZrO_2 were described earlier (22, 23). Helium and oxygen gas (Loosco, Amsterdam) were dried by BDH molecular sieve type 4A. Helium was further deoxygenated by BTS catalyst R-3-11 (BASF, Germany). Methanol was from Merck, analytical grade. For calibration of the gas-chromatographic analyses, CO and CO_2 gas (both Loosco, Amsterdam) a formaldehyde solution (Baker, analytical grade), and dimethyl ether (Matheson) were used.

Catalyst preparation. Supported vanadium oxide catalysts were prepared by passing a freshly prepared aqueous solution of NH_4VO_3 (1 wt%), acidified to pH = 4, through a bed of support particles (0.3-0.6 mm diameter). The catalysts were dried at 383 K (17 h) and calcined at 723 K (2 h). For further details see Part 1 of this series (22).

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X-ray fluorescence. The vanadium content of the catalysts was determined by X-ray fluorescence with a Philips 1410 X-ray spectrometer (26).

BET surface area measurements. Surface areas of the catalysts were determined as described previously (22).

Apparatus. Figure 1 shows the flow diagram of the apparatus used for methanol oxidation studies. Compressed helium and oxygen from cylinders were separately passed through purifying tubes. Both gases were dried with molecular sieves and helium was deoxygenated with a BTS catalyst. The gases passed through separate pressure controllers (PC) and pressure indicators (PI), then through flow controllers (FC) and indicators (FI) before mixing. Methanol was introduced by bubbling the He-O₂ mixture through a glass saturator filled with methanol. The saturator was immersed in a thermostat, which was usually kept at 286 K. Behind the saturator all stainless-steel tubing was heated to prevent condensation (dotted tubings in Fig. 1).

The reactor was a quartz tube (0.5 cm inner diameter and about 40 cm long) placed concentrically in a quartz tube of 1.0 cm inner diameter, on the outside of which an electric heating wire was wound. A fritted quartz disc in the reactor tube supported the catalyst bed. For all runs 0.2 g of catalyst (0.3–0.6 mm grain diameter) was used, mixed with 0.2 g of (inert) quartz

grains of similar size, in order to minimize exothermic effects. A quartz wool plug was tamped down on top of the catalyst to prevent fluidizing of the bed or loss of the catalyst. The catalyst bed height was usually about 1 cm. The reactor temperature was controlled by a chromel–alumel thermocouple (located with its tip in the catalyst bed) connected to a temperature controller. Manometers were placed before and after the reactor. A bypass system with a restrictive valve could be used to circumvent the reactor with equal restriction.

The feed gas consisted of approximately 72 vol% He, 24 vol% O₂, and 4 vol% methanol vapor. The total gas flow usually amounted to 40 ml (NTP) · min⁻¹.

Analyses were carried out with a Varian 3700 modular dual-column gas chromatograph connected to a chart recorder and an integrator (Infotronics). The columns were of stainless steel, each 1 m in length and $\frac{1}{8}$ in. outer diameter, filled with 60–80 mesh carbosphere support. Semiautomatic sampling was performed with an eight-way Carle microvolume switching valve with an analysis loop volume of 0.5 ml, which was placed in a valve oven kept at 450 K. The accuracy of this analytical procedure on the basis of carbon material balance was proven to be within 10%. Reaction temperatures were chosen in a random order rather than in a rising or falling order. In these results only the temperature region in

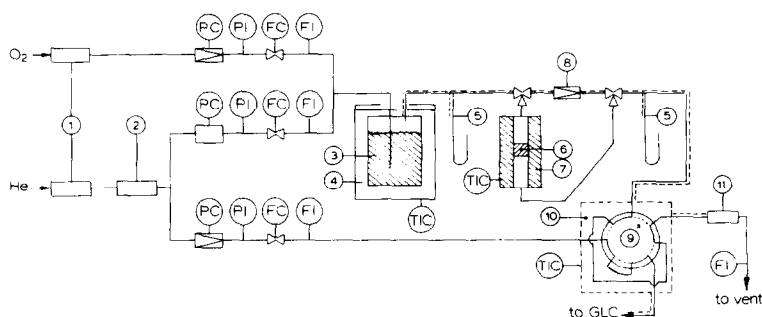


FIG. 1. Flow diagram of apparatus for methanol oxidation. 1 = tube with molecular sieve; 2 = tube with BTS catalyst R-3-11; 3 = vaporizer filled with pure methanol; 4 = thermostat; 5 = mercury manometers; 6 = reactor tube; 7 = tubular furnace; 8 = restriction valve; 9 = eight-way valve; 10 = valve oven; 11 = condenser and ---- = heated tubings.

which noticeable activity is observed, is considered. Therefore it was decided not to recalculate these activities to specific values based on the only slightly differing V contents. For every temperature the average of several steady-state activity measurements was calculated when the separate values did not differ by more than about 15%. In general, a steady state was reached within 15 min and at each temperature at least three measurements were performed. Within a total time of 48 h for a complete series of measurements no significant change in activity was observed.

RESULTS

The physicochemical properties and data of the supported and unsupported vanadium oxide catalysts were reported earlier (22–24).

The following catalysts, described and tested for CO oxidation (25), were tested here for methanol oxidation: unsupported V_2O_5 (prepared from NH_4VO_3), $V/\gamma-Al_2O_3$, V/CeO_2 , V/TiO_2 , V/ZrO_2 (where V indicates vanadium oxide monolayer) as well as the pure supports.

Unsupported V_2O_5 . Catalytic activity and selectivities of pure V_2O_5 are presented in Fig. 2. Formaldehyde is the main product up to 260°C, together with some dimethyl

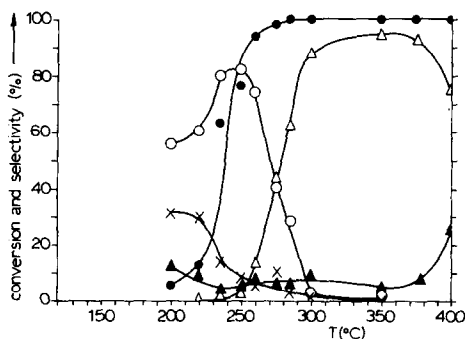


FIG. 2. Methanol oxidation over unsupported V_2O_5 ($S_{BET} = 9.5 \text{ m}^2 \text{ g}^{-1}$). ●, Total conversion (moles of methanol converted/moles of methanol fed) $\times 100\%$; x, selectivity to dimethyl ether; ○, selectivity to formaldehyde; △, selectivity to CO, and ▲, selectivity to CO_2 . Selectivities: (moles of methanol converted to product i /moles of methanol converted) $\times 100\%$.

ether and small amounts of CO and CO_2 . At 260°C formaldehyde production rapidly decreases in favor of carbon monoxide formation. From about 380°C the formation of CO decreases and that of CO_2 increases.

$\gamma-Al_2O_3$ and $V/\gamma-Al_2O_3$. Figure 3 shows the activity and selectivity patterns of $V/\gamma-Al_2O_3$ and pure $\gamma-Al_2O_3$. The pure carrier shows a high activity for dehydration of the methanol to dimethyl ether up to 330°C. At higher temperatures activity for CO and CO_2 becomes predominant. $V/\gamma-Al_2O_3$ shows up to 220°C high activity and selectivity to formaldehyde and only a slight selectivity to dimethyl ether. From 220°C formaldehyde production decreases, again in favor of a high activity and selectivity of CO up to 380°C. Above this temperature formation of CO drops and that of CO_2 rises.

CeO_2 and V/CeO_2 . Pure CeO_2 (Fig. 4) shows high selectivity to CO and CO_2 and no selectivity to other products. When a

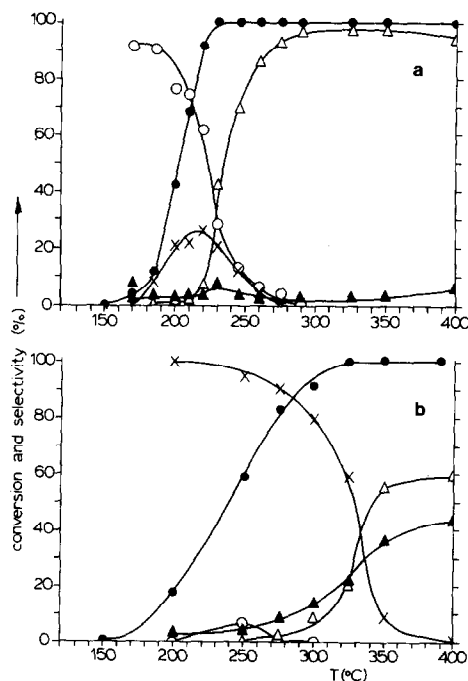


FIG. 3. Methanol oxidation over (a) $V/\gamma-Al_2O_3$ ($80 \text{ m}^2 \text{ g}^{-1}$, 6.8% V) and (b) $\gamma-Al_2O_3$ ($80 \text{ m}^2 \text{ g}^{-1}$). For symbols see Fig. 2.

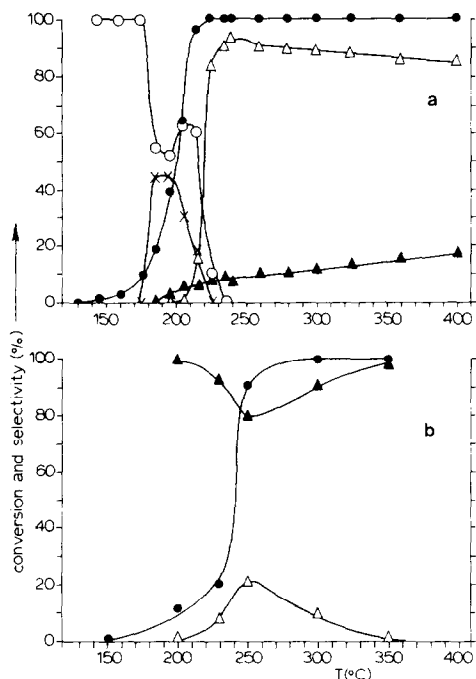


FIG. 4. Methanol oxidation over (a) V/CeO₂ (48 m² g⁻¹, 5.3% V) and (b) CeO₂ (48 m² g⁻¹). For symbols see Fig. 2.

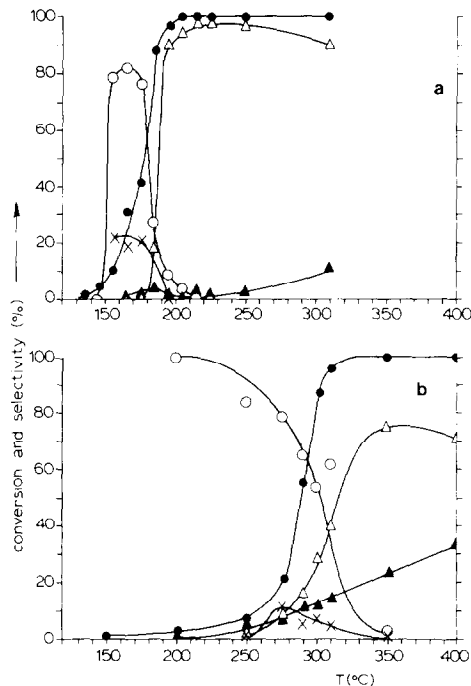


FIG. 5. Methanol oxidation over (a) V/TiO₂ (45 m² g⁻¹, 1.7% V) and (b) TiO₂ (45 m² g⁻¹). For symbols see Fig. 2.

monolayer of vanadium oxide is applied onto the CeO₂ the activity and selectivity patterns resemble those of V/γ-Al₂O₃. At low temperatures up to 210°C there is high activity and selectivity to formaldehyde, together with some dimethyl ether. Above 220°C is the main product, whereas above 250°C gradually more CO₂ is being formed at the expense of CO.

TiO₂ and V/TiO₂. At temperatures up to about 300°C the pure TiO₂ carrier (see Fig. 5) shows a minor dimethyl ether production together with a highly selective formation of formaldehyde. Above 300°C this selectivity falls very fast and total oxidation predominates, first to CO and at higher temperatures to CO₂.

The activity and selectivity patterns of V/TiO₂ resemble those of pure V₂O₅ and pure TiO₂, as regards the sequence of selectivities. However, the activity of the monolayer catalyst is larger, i.e., the temperature at which a comparable conversion occurs is significantly lower.

The V/TiO₂ was checked for diffusion limitation effects by calculating the Thiele modulus, m . The rate constant at a gas flow rate of 20 ml · min⁻¹ was calculated to be approximately 0.035 sec⁻¹. The effective diffusion coefficient of the TiO₂ used was determined to be 0.015 D_{gas} from measurements of CO₂ diffusion. With a diffusion coefficient of 1 cm² · sec⁻¹ for methanol in He and a radius of 0.5 mm of the catalyst grains this gives $m = 0.08$ indicating the complete absence of diffusion limitation.

ZrO₂ and V/ZrO₂. Pure ZrO₂ (Fig. 6) exhibits a high activity for the formation of CO and CO₂, with at higher temperatures a decrease of CO formation in favor of CO₂. Below 280°C some dimethyl ether was formed. No formation of formaldehyde was observed.

With V/ZrO₂, in the temperature range 150–175°C, a moderate activity was observed with formaldehyde as the main product, as well as a considerable amount of dimethyl ether. Above 180°C the selec-

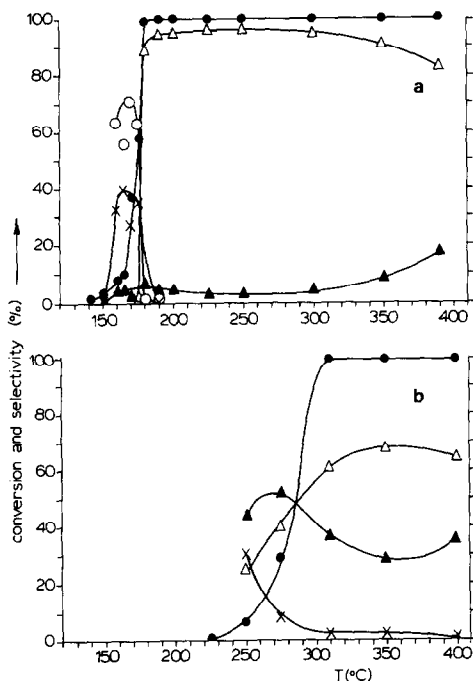


FIG. 6. Methanol oxidation over (a) V/ZrO₂ (107 m² g⁻¹, 4.3% V) and (b) ZrO₂ (156 m² g⁻¹). For symbols see Fig. 2.

tivity to formaldehyde decreases, whereas selectivity to CO increases, both very severely. Above 300–350°C more CO₂ is gradually formed, the amount of CO proportionally diminishing.

In Figs. 2 and 6 one can distinguish two temperature regions of different CO₂ production. In the temperature range of approximately 200–250°C (150–200°C for V/TiO₂ and V/ZrO₂) CO₂ is formed on every catalyst in a measurable (though in an absolute sense small) amount at a lower temperature than that at which CO is formed. At temperatures from 300–350°C, CO₂ is formed in large amounts at the expense of CO.

DISCUSSION

All activity and selectivity patterns of the unsupported and supported vanadia catalysts show the same features. At low temperatures, the small selectivity to dimethyl

ether rapidly decreases when the temperature is raised.

At the same, relatively low, temperatures a considerable amount of formaldehyde is formed, in all cases with higher activity and, at equal conversion, lower selectivity on the supported vanadia catalysts than on unsupported V₂O₅. Under mild conditions the two main reactions are (a) dehydration of methanol to dimethyl ether and (b) oxidation of methanol to formaldehyde and (slightly) to CO₂. Under more severe circumstances (higher temperatures) two further reactions take place, namely, (c) consecutive oxidation of the formaldehyde to carbon monoxide and (d) consecutive oxidation of CO and CO₂. These reactions will be discussed separately.

a. Dehydration of Methanol to Dimethyl Ether

As can be seen from Figs. 2 to 6 dimethyl ether formation predominates with pure γ -Al₂O₃. This is in agreement with the literature, where primary alcohols have been reported to yield ethers upon dehydration on alumina (27, 28), especially under mild conditions (low temperatures and low contact times). When conditions are severe, ethers are reported to react further with alumina to produce the same final products which are obtained by reaction of the corresponding alcohols. Thus the decrease in selectivity to ether, presented in Figs. 2–6, may be explained in terms of consecutive oxidation. When γ -Al₂O₃, with its intrinsic high selectivity for dehydration, is covered with a monolayer of vanadium oxide the dehydrating activity decreases significantly (Fig. 3). This, combined with evidence presented previously (22–24), is a further indication of the presence of a well-dispersed monolayer, covering the underlying γ -Al₂O₃. This is completely analogous to V/CeO₂, where the vanadia monolayer suppresses the activity for CO oxidation of the pure CeO₂ carrier (25).

*b. Oxidation of Methanol to
Formaldehyde and Direct Oxidation to
CO₂*

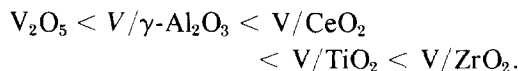
Methanol has been reported to be oxidized to formaldehyde presumably via an alcoholate bound to surface sites (9, 12). Ai (16) concludes these sites to be electron accepting (Lewis acidic) and proposes that they are anion vacancies. He further proposes electron-donating (Lewis-base) sites, suggested by him to be O²⁻ ions, to cause direct oxidation to CO₂ under the same mild circumstances. Miyata *et al.* (29) propose that CO₂ is formed directly via a formate intermediate.

It may be seen from Figs. 2–6 that basic oxides like ZrO₂ and in particular CeO₂ indeed yield CO₂ at temperatures as low as 200–250°C. Here no selectivity to formaldehyde is observed. This may point to the predominance of basic sites over acidic sites on ZrO₂ and CeO₂, whereas on TiO₂ sites with selectivity to formaldehyde predominate. On γ -Al₂O₃ an interpretation in terms of acid/base sites fails because of its high dehydration activity.

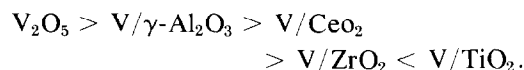
Ai's acid/base model suffers from the fact that it is difficult to quantify the number and strength of the basic and acidic sites and to identify these unambiguously. An interpretation in terms of acid/base properties of this type of oxidation seems to be somewhat doubtful. In the first place a metal ion like Al³⁺ is a relatively strong Lewis acid (i.e., electron acceptor) without, however, having oxidizing properties like V⁵⁺ or V⁴⁺. In the second place for metal ions with variable valency the acid-base properties change with the oxidation state, e.g., Cr⁶⁺ is strongly acidic and Cr³⁺ is basic.

The reducibility of an oxidic catalyst can be defined in several ways. For example, this can be expressed by the temperature where reduction by hydrogen begins in thermogravimetric (TG) experiments or where activity in CO oxidation starts to become measurable.

In both cases the order of reducibilities has been shown (25) to be



The onset temperatures of hydrogen reduction as determined by TG (25) are given in the second column of Table 1. The table shows that the order of selectivity to formaldehyde is



With V/TiO₂ as an exception it can be concluded that selectivity increases when reducibility decreases. This observation is in agreement with the findings of Sachtler *et al.* (30) who stated that activity and reducibility run parallel (as shown in this case by the parallelism of the reduction temperature and the temperature at 50% conversion) and that selectivity and reducibility (i.e., ease of removal of oxygen) run antiparallel.

Also Boreskov (31) concluded that an increase in the energy of oxygen bonding (i.e., a decrease in ease of oxygen removal) reduces the rate of methanol oxidation on oxidic catalysts and increases the selectivity to formaldehyde.

The results of a study (24) on the reducibility of vanadium oxide monolayer catalysts, conducted by TPR, leads to the assumption that the reducibility of a catalyst is mainly influenced by catalyst-support interactions. These interactions can be related to the parameter z/a , i.e., the ratio of the carrier cation charge to the sum of ionic radii of carrier cation and oxide anion (22, 32, 33). From Table 1 it can be seen that, except for V/TiO₂, the parallelism between reducibility and z/a on the one hand and the antiparallelism between selectivity and z/a on the other hand holds rather well.

V/TiO₂ exhibits a selectivity to formaldehyde which is larger and a reducibility which is lower than expected on the basis of its z/a parameter. This irregularity may

TABLE I
Results on Methanol Oxidation

Catalyst	Onset temperature of H ₂ reduction (25) (°C)	Reaction temperature at 50% total conversion (°C)	Selectivity to formaldehyde at 50% total conversion (%)	z/a of carrier cation (22)
V ₂ O ₅	460	240	82	—
V/ γ -Al ₂ O ₃	360	203	81	1.55
V/CeO ₂	360	200	58	1.69
V/TiO ₂	320	178	70	1.99
V/ZrO ₂	180	175	50	1.79

be ascribed to, for instance, structural factors (24, 34) and to the different type of active sites present on this catalyst (25). The larger selectivity of V/TiO₂ in relation to its reducibility may also be connected with the fact that TiO₂ is the only support which shows selectivity to formaldehyde when no vanadia is present. As yet no conclusive explanation can be given for this discrepancy.

c. Consecutive Oxidation of Formaldehyde to CO

From Figs. 2-6 it is evident that formaldehyde (and dimethyl ether) production falls sharply owing to a steep rise in formation of CO with increasing temperature. This points to a consecutive oxidation of formaldehyde to carbon monoxide, which may proceed via formic acid as an intermediate. Because formic acid was never detected in our experiments it is either not an intermediate or it decomposes rapidly to CO (35).

d. Consecutive Oxidation of CO to CO₂

From Figs. 2-6 it can be seen that at higher temperatures CO₂ is formed at the expense of CO. Thus it is plausible to suppose that CO is consecutively oxidized to CO₂. In Fig. 7 the selectivities to CO₂ for the methanol oxidation over the supported monolayer catalysts are presented together with the activities for the oxidation of CO to CO₂ obtained in a previous study (25).

This figure shows that the temperatures at which the formation of CO₂ in methanol oxidation starts to increase are close to those at which CO alone starts to be oxidized to CO₂ (25). This holds especially for V/ γ -Al₂O₃ and for V/ZrO₂. For V/CeO₂ and V/TiO₂ the former temperatures are somewhat lower than the latter. In the previous study (25) it was also observed that V/CeO₂ and V/TiO₂ exhibited higher activity for CO oxidation after reduction by H₂ and subsequent reoxidation by O₂. On

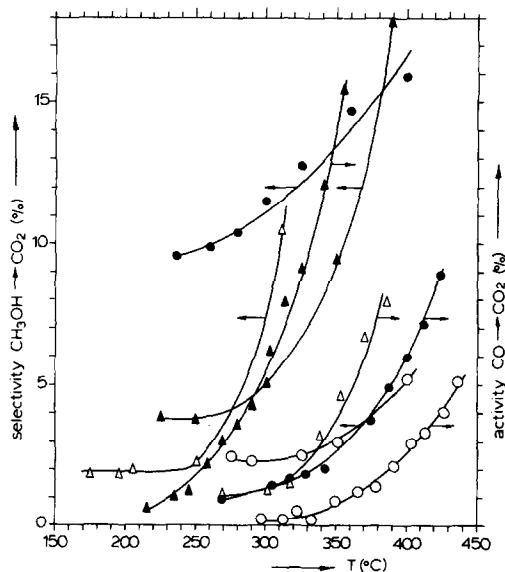


FIG. 7. Selectivity to CO₂ for methanol oxidation and activity for CO oxidation to CO₂ over V/ γ -Al₂O₃ (○), V/CeO₂ (●), V/TiO₂ (△), and V/ZrO₂ (▲), plotted vs temperature (°C).

the other hand V/ γ -Al₂O₃ and V/ZrO₂ were insensitive for reduction/reoxidation treatment.

This seems to be also valid for methanol oxidation: the reduction/reoxidation is then caused by the methanol/oxygen gas mixture, thus creating vacancies and active sites prior to consecutive oxidation to CO₂.

In conclusion it may be supposed that at higher temperatures CO₂ is formed from produced CO via a reduction-reoxidation mechanism.

CONCLUSIONS

On supported and unsupported vanadia the catalytic oxidation of methanol takes place in two stages: (1) at moderate temperatures methanol is both dehydrated to dimethyl ether and selectively oxidized to formaldehyde; (2) at higher temperatures consecutive oxidation of the initial reaction products (ether and formaldehyde) to CO and consecutive oxidation of CO to CO₂ proceeds.

In general, the selectivity to formaldehyde increases with decreasing reducibility of the catalyst (V/TiO₂ being exceptional); this is a function of catalyst-support interactions and can be related to the z/a ratio of the carrier cation.

ACKNOWLEDGMENTS

Thanks are due to Mr. E. Bijsterbosch and Miss. M. Jovašević for performing part of the experimental work. Professor J. W. Geus, University of Utrecht, the Netherlands, is acknowledged for his comments on the manuscript.

P.D.C. wishes to thank IAESTE for financial support. This study was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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