

Catalytic Activity of Vanadates in Oxidation of Methanol

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The investigations of catalytic activities of V_2O_5 -NiO, V_2O_5 -Fe₂O₃, and V_2O_5 -Co₃O₄ systems in the reaction of methanol oxidation to formaldehyde show much higher selectivities for mixed than for pure oxides. The highest CH₂O yield was obtained for catalysts with atomic ratios V/Me = 1.

Besides methanol oxidation by the conventional flow method at 310°C on catalysts of different V:Me ratios, measurements for the three V/Me = 1 systems by the pulse method without oxygen were carried out, showing different reaction mechanisms, involving H₂ evolution. In case of the V-Ni catalyst, which is the most selective one, no H₂ was found in the reaction products.

Infrared spectra taken of the 1:1 catalysts before and after 2 hr of methanol oxidation at 410°C show different stabilities of the V = O bond, which is most constant in the V-Ni system. The resulting structure modifications are most significant in the Me-O bond region.

INTRODUCTION

The activity of the oxide systems V_2O_5 -Fe₂O₃, V_2O_5 -Co₃O₄, and V_2O_5 -NiO in the reaction of selective oxidation of methanol to formaldehyde has not hitherto been investigated.

The commercial production of formaldehyde is based on the MoO₃-Fe₂(MoO₄)₃ catalyst. Results of studies on this catalyst have been summarized by Pernicone (1). It seems that the ability for selective oxidation is connected with the presence of the Mo=O terminal bond, which has the character of a labilized double bond (2, 3). The trivalent cations have a promoting influence on the redox process which is carried out by the Mo⁶⁺ ions (4). To in-

vestigate the reaction mechanisms, reduction of the catalysts has been studied by spectral methods (5-7). It was found that catalysts active in the oxidation of CH₃OH to CH₂O must possess an adequate reducibility. They must also contain acid sites (8). Boreskov (9) correlated the catalytic activity of oxides of the elements of the IVth period with their activity in the homomolecular exchange of oxygen. On this basis Trifirò and Pasquon (4) found a lack of activity for CO oxidation at 350°C and a high selectivity of CH₃OH oxidation for systems with a Mo=O bond, such as Fe, Co and Ni molybdates and MoO₃, which show a low rate of homomolecular oxygen exchange at 300°C. On the other hand, pure Fe₂O₃, Co₃O₄, and NiO oxides, showing a much higher homomolecular oxygen

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TABLE 1
The BET Surface Area and Oxygen Content of Mixed Oxides of Different Composition

Atomic ratios $\frac{V}{V + Me}$ (%)	V_2O_5-NiO		$V_2O_5-Fe_2O_3$		$V_2O_5-Co_3O_4$	
	BET surface area, S_{BET} (m^2/g)	Oxygen content (%)	BET surface area, S_{BET} (m^2/g)	Oxygen content (%)	BET surface area, S_{BET} (m^2/g)	Oxygen content (%)
100	4.0	40.0 \pm 1.9	4.0	40.0 \pm 1.9	4.0	40.0 \pm 1.9
95	4.0	—	4.0	—	4.4	—
90	3.7	40.8 \pm 2.4	3.8	40.7 \pm 2.4	4.5	30.7 \pm 3.1
80	3.0	—	3.8	—	4.9	—
70	2.8	—	5.8	—	4.9	—
60	2.6	—	7.8	—	4.8	—
50	2.6	36.6 \pm 1.1	8.5	37.7 \pm 0.9	4.8	35.7 \pm 0.8
34	4.1	—	6.0	—	4.5	—
20	5.2	32.5 \pm 2.2	4.8	35.3 \pm 1.6	4.4	—
14	5.0	—	4.0	—	4.0	31.5 \pm 2.4
0	4.9	19.8 \pm 1.2	3.8	28.8 \pm 0.7	3.5	24.6 \pm 1.6

exchange rate, are active in CO oxidation and only very slightly selective in the CH_3OH conversion. V_2O_5 lies between these two groups of compounds with regard to the above properties. It also possesses a terminal group of double bond character, which is supposed to be an active site (10).

Bliznakov *et al.* (11) studied tungstates of metals of the IVth period with regard to their catalytic properties of methanol oxidation to formaldehyde. The highest reaction yield was found for ferric tungstates; however, their activity was much lower than that of ferric molybdates.

In the present work the activities for methanol oxidation to CH_2O of three mixed vanadium catalysts have been investigated, and studies on the reduction of the catalysts were carried out.

EXPERIMENTAL METHODS

Materials

Thirty-three catalysts with different atomic ratios $V/(V + Me)$ ($Me = Fe, Co, Ni$) were prepared. To $Ni(NO_3)_2 \cdot 6H_2O$

solutions V_2O_5 was added; the mixture was evaporated and calcined at $600^\circ C$ until the loss of nitrogen oxides. After grinding, the catalysts were activated by calcination at $600^\circ C$ for 6 hr.

Table 1 gives the composition of the catalysts, their BET surface areas and their oxygen contents. The last were determined on a EAO-202 Balzers Exhalograph.

Measurements of x-ray diffraction were made by the Debye-Scherrer method using a Hitachi instrument with Cu-targets for V-Co and V-Ni catalysts and Co-targets for the V-Fe systems. Infrared spectra were recorded on a Hitachi spectrometer: KBr discs were used.

RESULTS

Measurement of Catalytic Activity and Selectivity

Oxidation of methanol with air was carried out by the conventional flow method at $310^\circ C$. The ratio of catalyst weight to methanol flow rate was 3.78 g-hr/mol. The methanol concentration in the mixture

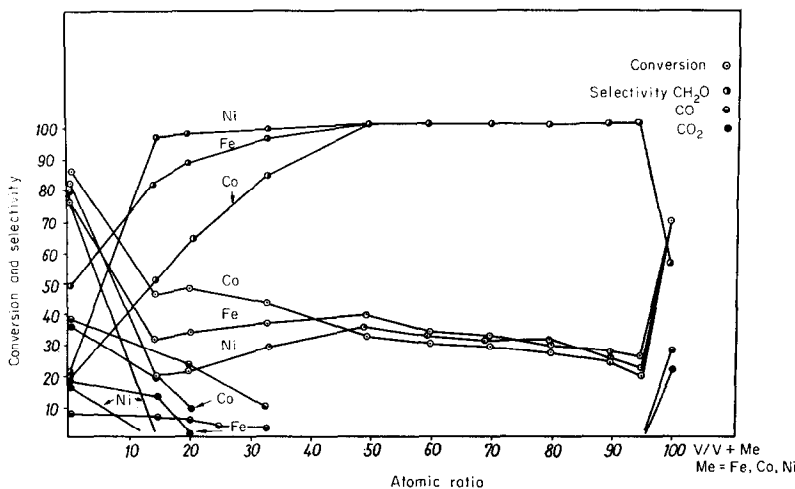


FIG. 1. Effect of catalyst composition on the overall conversion and selectivity of methanol oxidation at 310°C. $W/F = 3.78$ g-hr/mole.

with helium and oxygen was 44%, the mole ratio CH_3OH/O_2 being 2.2. The activity data were taken after 1 hr of run. After that time the activity values were constant during the next 12 hr. The reaction products were analyzed by chromatographic methods. Methanol, formaldehyde and water were determined on a 3-m column packed with Flusin T with 30% triacetine. The working temperature was 110°C. CO and CO₂ were determined on two columns

with molecular sieve 13 X and active carbon, respectively.

The values of the overall methanol conversion and of selectivities are plotted with respect to catalyst composition in Fig. 1.

Methanol-Catalyst Reaction without Oxygen

Oxidations of methanol by the catalysts were carried out in a pulse reactor. In each

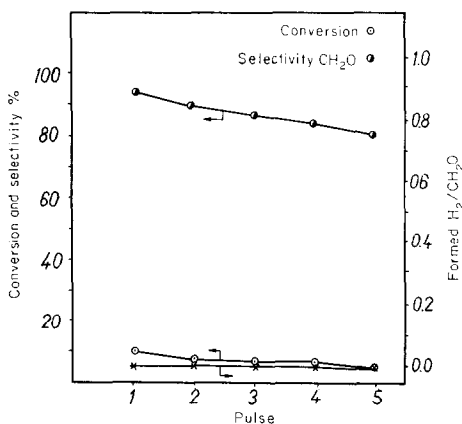


FIG. 2. The overall conversion and selectivity of the V:Ni = 1 catalyst in the pulse reactions without oxygen at 300°C.

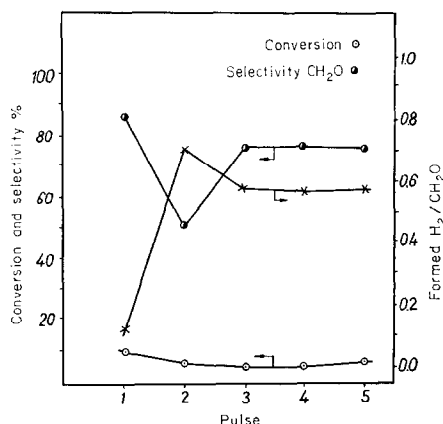


FIG. 3. The overall conversion and selectivity of the V:Fe = 1 catalyst in the pulse reactions without oxygen at 290°C.

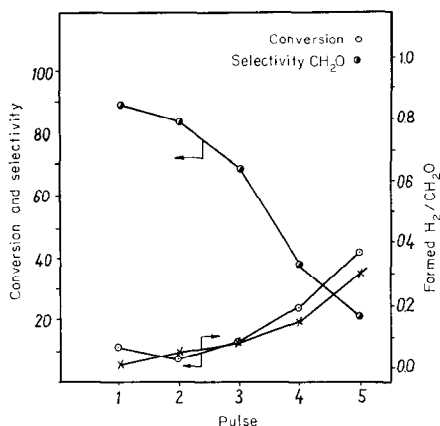


Fig. 4. The overall conversion and selectivity of the V:Co = 1 catalyst in the pulse reactions without oxygen at 340°C.

run 84.5 μmol CH_3OH was carried by nitrogen with a velocity of 100 ml/min from a volume of 5.1 ml to 0.5 g of the

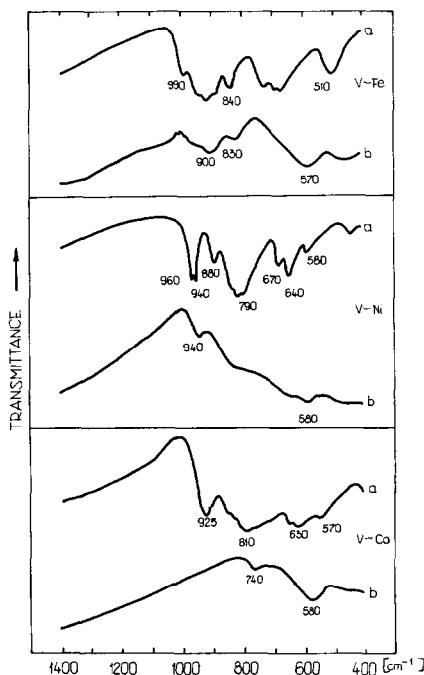


Fig. 5. Infrared spectra of V:Me = 1 catalysts (a) before oxidation of methanol, (b) after 2 hr of methanol oxidation at 400°C in the flow method.

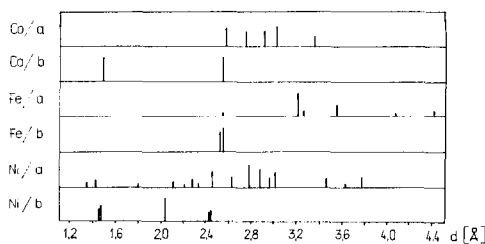


Fig. 6. X-Ray diffraction patterns of V:Me = 1 catalysts (a) before the oxidation of methanol, (b) after 2 hr of methanol oxidation at 400°C.

catalyst. The results are shown in Figs. 2, 3, 4.

Studies of Structure Changes during Methanol Oxidation

The catalysts with atomic ratios V:Me = 1 were investigated for structure modifications. Infrared spectra and X-ray patterns were recorded before and after 2 hr of methanol oxidation in the flow method (Figs. 5 and 6).

DISCUSSION

The correlation in Fig. 1 between the catalyst composition and the overall conversion of CH_3OH as well as selectivity of oxidation to CH_2O shows that the catalytic properties of mixed oxides are not linear functions of the properties of the components, similarly as for Mo-Fe systems (12). The mixed catalysts have a much higher selectivity. The catalysts with an atomic ratio V:Me = 1 have the highest conversion of methanol to formaldehyde. Pure V_2O_5 , Co_3O_4 , Fe_2O_3 , and NiO oxides show a much higher overall conversion than mixed oxides. The addition to V_2O_5 of even small amounts (a few percent) of Co_3O_4 , Fe_2O_3 , or NiO causes a large decrease of the overall conversion but a significant increase of selectivity, which in the range of 5–50% atom Me (for Ni systems even in the range of 5–85%) amounts to 100%.

The results of experiments obtained for the reaction without oxygen by the pulse method (Figs. 2, 3, 4) show differences between the methanol dehydrogenation mechanisms on different mixed catalysts with atomic ratio V:Me = 1.

The high selectivity of the V-Ni catalyst and the lack of hydrogen as a reaction product may be explained in terms of very reproducible oxygen active centers. If the dehydrogenation of methanol is occurring with simultaneous dehydration of the catalyst, there would be no hydrogen in the gas phase. The almost constant values of activity and selectivity of the V-Ni catalyst (Fig. 2) suggest that OH groups formed by the CH₃OH dehydrogenation are abstracted from the catalyst and the oxygen defects are quickly replaced by oxygen atoms from the lattice, preventing the adsorption of formaldehyde and its dehydrogenation.

The V-Fe catalyst shows a different reaction mechanism. The constant selectivity in successive pulses demonstrates the same high ability to regenerate the active centers as in case of the Ni catalysts. But the large amount of hydrogen in the reaction product suggests that the dehydrogenation of methanol by the V-Fe catalyst is exerted by oxygen atoms which are not abstracted from the catalyst surface.

The ir spectra of the V-Ni and V-Fe catalysts before reaction with methanol are quite different even in the range of V-O bonds (Fig. 5). The V-Ni phase spectrum has a discrete band at 940 cm⁻¹ due to the asymmetric stretching vibration mode of V=O (10). In case of the V-Fe catalyst the bands in that vibration region have a different character.

The spectrum of the V-Co catalyst shows the same nature of the V=O bond as the V-Ni system. The increase of the H₂ yield from one pulse to another may be explained by assuming that the active oxygen centers

are not as quickly regenerated as in the Ni catalyst. While the number of oxygen defects increases, more aldehyde molecules are adsorbed and decomposed with simultaneous H₂ evolution, which is in agreement with the decreasing selectivity.

The results obtained lead to the conclusion that the lack of oxygen defects is the reason for selective oxidation of methanol to formaldehyde. Supposing that oxygen defects are the cause for the dissociative oxygen chemisorption, we may relate our work also to the conclusion of Haber (13) that the oxides which have the ability for selective oxidation are only those for which no dissociative oxygen chemisorption is taking place.

The spectroscopic investigations of structural changes caused by the methanol oxidation show, that the V=O bond is directly involved in the reaction mechanism, which is proved by the disappearance of the appropriate band in the V-Co catalyst spectrum and by the lowering of the band intensity in the V-Ni catalyst spectrum. Nevertheless in the V-Ni and V-Fe systems the vanadium-oxygen bonds are quite stable. More significant spectra variations are observed in the range of Me-O bonds.

The spectra of catalysts before the reaction are characteristic for new phases with no bands of the single oxides. The spectra taken after the reaction show at lower wavenumber values the presence of CoO, NiO, and Fe₂O₃ (14). The same changes are observed on the X-ray patterns (Fig. 6).

The above results, which are in agreement with the experiments of Trifirò and Pasquon (4), prove that the catalyst double bond is more stable than the Me-O bond system in mixed oxide catalysts.

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