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Methanol Oxidation on K_2SO_4-Promoted Vanadium Pentoxide: Activity, Reducibility, and Structure of Catalysts

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The promoting action of K_2SO_4 on unsupported V_2O_5 catalysts used for the oxidation of methanol to formaldehyde has been studied in a microscale fixed-bed reactor in the temperature range 550 to 750 K. The K_2SO_4 content of the catalysts was varied between 0 and 40 mol%. Selectivities to formaldehyde were higher for all catalysts containing K_2SO_4. Highest selectivities (>95%) were found for catalysts containing 10 and 20% K_2SO_4. TPR measurements showed that starting temperatures for catalyst reduction by hydrogen were lowered by more than 150 K when the K_2SO_4 content was increased from 0 to 40%. TPR profiles of the catalysts measured after steady-state methanol oxidation indicated an increasingly reduced state of the catalysts with higher K_2SO_4 contents. Structural investigations on the promoted vanadium oxides showed that they are composed of two phases: pure V_2O_5 consisting of well-developed plate-like grains and agglomerates of needle-type $5V_2O_5 \cdot 3K_2SO_4$ crystals with diameters of approximately 1 μm.

INTRODUCTION

The promoting action of the addition of K_2SO_4 to V_2O_5 has been the subject of several studies. Increased conductivity, reaction rate of oxygen with hydrogen, and rate of oxygen isotope exchange demonstrated the effect of the K_2SO_4 promoter on the oxygen mobility of such mixed catalysts (*1*). Oxygen isotope exchange experiments have also been performed to establish the promoting action of different alkali metal sulfates (*2*) and various potassium compounds (*3*) on vanadium catalysts.

Tarama *et al.* (*4*) investigated the properties of the V_2O_5–K_2SO_4 system using X-ray, ESR, infrared, and magnetic susceptibility measurements. They explained the promoter action of K_2SO_4 by a weakening of the V=O bond in the V_2O_5 lattice and a lowering of the melting point of the mixed catalysts. The latter property plays a decisive role for SO_2 oxidation. Sharma *et al.* (*5*) investigated the structural properties of silica-supported V_2O_5–K_2SO_4 catalysts. X-Ray and electron microscopy results indicated the coexistence of pure V_2O_5 and K_2SO_4 without any interaction. The authors observed that the addition of K_2SO_4 led to a preferential growth of needle-type V_2O_5 which was most active for the selective oxidation of methanol to formaldehyde.

Methanol oxidation kinetics on V_2O_5-containing catalysts have been studied by several authors (*6–9*). Data analysis has normally been based on the reduction–oxidation mechanism proposed by Mars and van Krevelen (*10*). These authors assumed that the hydrocarbon is adsorbed on the catalyst which then releases oxygen and, in a second step, becomes reoxidized with oxygen from the reactant gas mixture. The performance of multiple oxidation state catalysts for partial oxidation reactions is thus closely related to their ability to take up and release lattice oxygen.

With this in mind we have investigated the reduction behavior and the structure of K_2SO_4-promoted V_2O_5 catalysts. The relationship of these properties of the catalysts

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with their activity and selectivity for partial oxidation was examined using the oxidation of methanol as a model.

EXPERIMENTAL

Catalysts

Ammonium metavanadate (Fluka, p.a.) and potassium sulfate (Merck, p.a.) were ground to particle sizes lower than 150 μm. A wet paste was obtained by mixing the required portions of these two compounds with water. The paste was slowly dried and then heated for 2 h at 200, 450, and, 700°C and subsequently allowed to cool in the oven. Catalysts were ground and the fraction with grain sizes between 100 and 200 μm was used for the experiments.

Catalyst Characterization

Physical and chemical properties of the catalysts were characterized by temperature-programmed reduction (TPR), X-ray diffraction techniques, scanning electron microscopy coupled with energy dispersive analysis of X-rays (EDAX), transmission electron microscopy coupled with selected area electron diffraction, thermogravimetric analysis (TG), and gas adsorption measurements (BET).

The apparatus used for the TPR measurements has been described elsewhere (*11*). The standard conditions for the TPR experiments were: amount of sample, 222 μmol V_2O_5; heating rate, 0.155 K/s; hydrogen concentration in nitrogen, 6 mol%; total flow rate, 1.25 ml/s.

X-Ray diffraction experiments were carried out with a Philips diffractometer (Cu$K\alpha$ radiation, nickel filter) and a Guinier-IV camera (Cu$K\alpha_1$ radiation, nickel filter, Johansson monochromator).

The electron microscope investigations were performed on a scanning electron microscope (Stereoscan-SI, Cambridge Instruments) with an EDAX analyzer and on a transmission electron microscope (JEOL-200 CX).

Thermogravimetric measurements were conducted with a Mettler thermoanalyzer TA 2000C using a 20% hydrogen/nitrogen (1 ml/s) gas mixture for the reduction experiments. The heating rate used was 0.167 K/s and the sample weight 47 mg.

Specific surface areas of the samples were determined by BET adsorption measurements using krypton at 77 K. Calculations were based on a cross-sectional area of 19.5 Å^2 for a krypton atom.

Methanol Oxidation

Oxidation experiments were carried out in a fixed-bed reactor of 18 cm length and 2 cm inner diameter. The Pyrex reactor was installed in the oven of a gas chromatograph for accurate temperature control. Temperatures in the catalyst bed were measured by a NiCr/Ni thermocouple of 0.5 mm diameter. Nitrogen and air were fed to the reactor without further purification. Methanol was dosed by a high-precision infusion pump (Infors Precidor, Type 5003) and mixed with air in an evaporator before entering the reactor. To avoid condensation of reactants and products, the tubing between the reactor outlet and the automatic gas sampling valve was heated to 100°C.

Procedure. The experiments were started by heating the catalyst in air (4.6 ml/s) to the desired reaction temperature. After maintaining these conditions for at least 30 min the infusion pump and the automatic sampling valve were turned on. Data collection was started after steady-state conditions were attained. The experiments were conducted under the following standard conditions: amount of catalyst, 1.48 g; particle size range of catalyst, 100–200 μm; feed rate air, 188 μmol/s; feed rate methanol, 16.4 μmol/s; total pressure, 106 kPa. The catalysts were always heated to 700 K in an air stream for 1 h after termination of an experiment. The sequence of selected reaction temperatures was random. The temperature for the last experiment performed with a particular catalyst charge was selected to give a conversion of about 0.5. After terminating this experiment the methanol/air feed was immediately replaced by nitrogen and the sample rapidly cooled to room temperature and kept under argon until it was further used.

Analytical procedure. The product gas was analyzed for nitrogen, oxygen, methanol, formaldehyde, and water by periodic injection of the reactant gas mixture into a gas chromatograph (Carlo Erba, Model 452 GI). Nitrogen and oxygen were separated with a molecular sieve column (5A) at 50°C. Methanol, formaldehyde, water, and air were separated by means of a Poropak Type T column at 147°C. The gaseous total oxidation products, CO and CO_2, were analyzed by the following methods: carbon dioxide was determined gravimetrically by passing the effluent gases through an ammonia solution for a fixed time and measuring the weight of the precipitated barium carbonate, after barium chloride was added to the solution. The carbon monoxide concentration was measured periodically by means of Dräger detector tubes.

Conversion, selectivity, and yield are defined as (ME, methanol; FA, formaldehyde):

$$\text{Conversion } X = \frac{\text{moles ME reacted per min}}{\text{moles ME fed per min}}$$

$$\text{Selectivity } S = \frac{\text{moles FA formed per min}}{\text{moles (FA + CO + CO}_2\text{) formed per min}}$$

$$\text{Yield } Y = X \cdot S.$$

The total fraction of carbon atoms analyzed ranged from 90 to 100% of the carbon atoms fed to the reactor. No correlation between the accuracy of the total carbon balance and conversion or selectivity could be observed. Thus, the inaccuracies were attributed to the experimental errors caused by the combination of the different analytical methods used.

RESULTS

Characterization of Fresh Catalysts

The TPR profiles measured for the fresh V_2O_5 samples with different K_2SO_4 contents are presented in Fig. 1. Reduction profiles obtained after use of the catalysts for methanol oxidation are also included in this figure and will be discussed later on in this paper. Up to five maxima in the hydrogen consumption rate can be distinguished when the K_2SO_4 content is increased. The beginning of the hydrogen consumption is lowered from 850 K for the pure V_2O_5 catalyst to approximately 700 K for the catalyst containing 40% K_2SO_4. The total hydrogen consumption can be separated into a low- and a high-temperature region. Integration of the hydrogen consumption rate from the low-temperature end of the profiles to the markers (see Fig. 1) gives hydrogen uptakes ranging from 243 to 267 μmol H_2. Individual values for the samples A to E are listed in Table 1 together with other properties of the fresh catalysts. The mean hydrogen consumption for the low-temperature part was 254 μmol which is in good agreement with the expected value of 222 μmol H_2 calculated for the reduction of all the

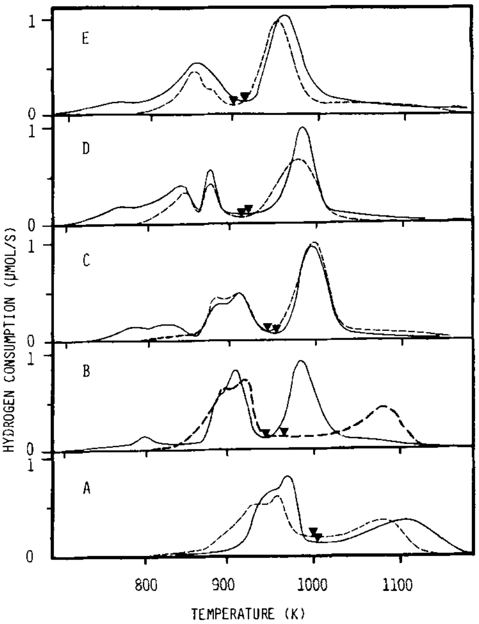

FIG. 1. Comparison of TPR profiles before (—) and after (---) steady-state methanol oxidation (integral hydrogen consumptions were determined up to the points marked in the TPR profiles (▼)).

TABLE 1

Characterization of Catalysts before and after Use in Methanol Oxidation

Sample	K_2SO_4 content (mol%)	BET surface area (m^2/g)	$T_{2.5}$ (K)	Hydrogen consumption[a] of fresh catalysts (μmol)	Hydrogen consumption[a] of used catalysts (μmol)	Mean oxidation number of the vanadium[b]
A	0	0.4	939	267	258	5.02
B	10	1.1	839	245	238	4.94
C	20	1.2	779	243	193	4.76
D	30	1.6	773	249	156	4.61
E	40	1.7	764	266	145	4.57

[a] Hydrogen consumption for low-temperature part of the TPR profile (see Fig. 1).

[b] A mean hydrogen consumption of 254 μmol was assumed for the reduction of all V^{5+} to V^{4+}.

V^{5+} to V^{4+}. Consequently, the low-temperature part can be ascribed to the reduction of the V^{5+} to V^{4+}, whereas the high-temperature peak shows further reduction of the V^{4+} to V^{3+} and partial reduction of the sulfate.

The weight loss during reduction of the catalysts was measured by thermogravimetry. As a quantitative measure for the reducibility of the catalysts, we have listed in Table 1 the temperatures ($T_{2.5}$) at which the loss of the catalyst weight due to reduction amounted to 2.5%. The thermogravimetric measurements confirmed that at higher temperatures also part of the K_2SO_4 was reduced under the conditions used.

X-Ray analysis indicated that the fresh samples, B, C, and D consisted of two phases, V_2O_5 (*12*) and $5V_2O_5 \cdot 3K_2SO_4$ (*13*). The intensities of the reflections of the mixed phase increased as the content of K_2SO_4 was increased. Sample E showed only the reflections of $5V_2O_5 \cdot 3K_2SO_4$. These results are in accordance with the phase diagram of the V_2O_5–K_2SO_4 system given by Hähle and Meisel (*13*).

The grain morphology of the catalysts changed significantly from pure V_2O_5 (catalyst A) to the mixed phase $5V_2O_5 \cdot 3K_2SO_4$ (catalyst E). The pure V_2O_5 consisted of well-developed plate-like grains as described elsewhere (*14*). Figure 2 depicts the morphology of catalysts C and E. Catalyst C consisted of both plate-like V_2O_5 and ag-

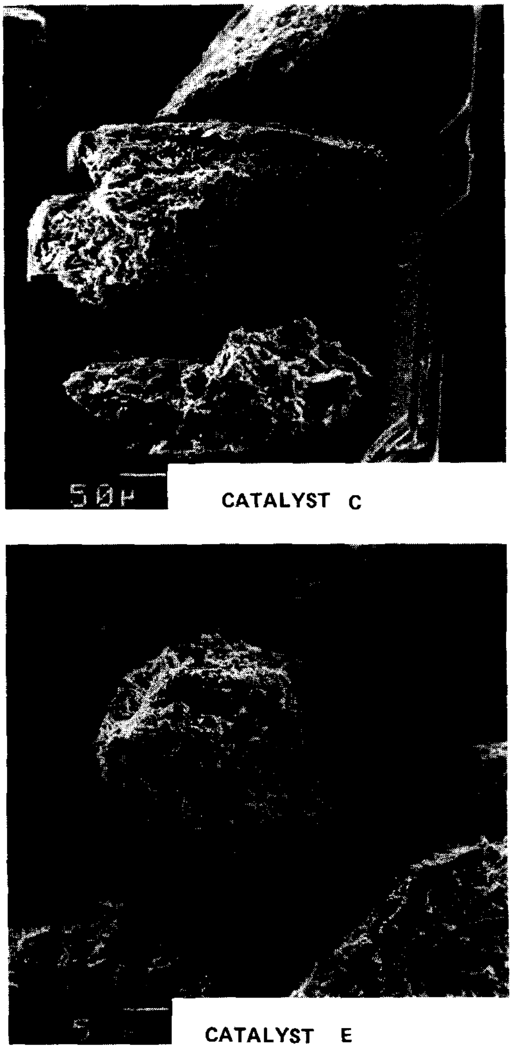

FIG. 2. Scanning electron micrographs of catalyst samples C and E.

glomerates of small needles of $5V_2O_5 \cdot 3K_2SO_4$. EDAX analysis of the plate-like grains did not give any indication for the presence of potassium in these grains. The existence of V_2O_5 crystallites in the catalysts A, B, C, and D was confirmed by transmission electron microscopy and selected-area electron diffraction. The interpretation of the electron diffraction patterns of the phase $5V_2O_5 \cdot 3K_2SO_4$, however, turned out to be difficult, as no data on the unit cell dimensions of this phase are yet available. The structure of this phase is presently being investigated in our laboratory.

Finally, it should be noted that the changes in grain morphology of the catalysts A to E resulted in a continuous increase of the BET surface areas of the catalysts from 0.4 to 1.7 (Table 1).

Methanol Oxidation

The effect of K_2SO_4 addition on the catalytic properties of the vanadium catalysts was investigated using the vapor-phase oxidation of methanol as a test reaction. All experiments were run under the standard conditions given under Experimental. The only products formed were formaldehyde, water, CO, and CO_2. At low conversions, CO was the only by-product. At high conversions, up to 2% of the methanol fed to the reactor was converted to CO_2.

Figure 3 illustrates the temperature dependence of conversion and selectivity of catalysts A, B, and E. Note that the conversion curve is steepest with pure V_2O_5 and becomes less steep with increasing promoter content. The selectivity of the promoted catalysts (B and C) is higher than that for pure V_2O_5. Similar behavior was also observed for catalysts C and D. The reaction behaviors of all catalysts are compared on the basis of different criteria in Table 2.

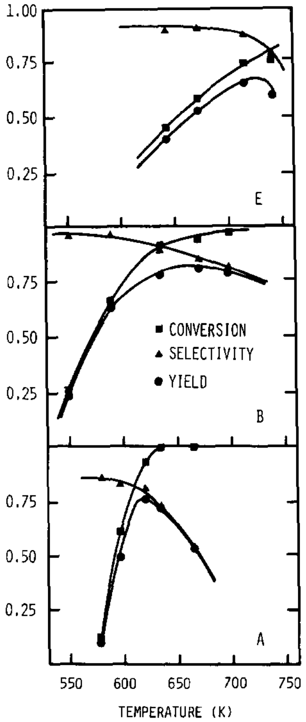

FIG. 3. Effect of reaction temperature on conversion, selectivity, and yield for methanol oxidation with pure V_2O_5 (catalyst A) and with catalysts containing 10% (catalyst B) and 40% (catalyst E) K_2SO_4.

Characterization of the Catalysts after Use for Methanol Oxidation

Figure 1 illustrates the changes in the TPR profiles of the five catalysts after use for methanol oxidation. The starting temperatures of reduction were shifted to lower

TABLE 2

Effect of Catalyst Composition on Activity (T_{50}), Selectivity (S_{50}), and Maximum Yield (Y_M) for the Oxidation of Methanol

Sample	T_{50}[a] (K)	S_{50}[b]	Y_M[c]
A	591	0.84	0.76
B	576	0.97	0.82
C	592	0.97	0.84
D	660	0.95	0.73
E	652	0.92	0.67

[a] Temperature required for a conversion of 0.5.

[b] Selectivity to formaldehyde at a conversion of 0.5.

[c] Maximum yield of formaldehyde.

temperatures for the used V_2O_5 (sample A). In contrast, the onset temperatures for reduction were higher for the promoted catalysts (samples B to E). Integral hydrogen consumptions for the low-temperature parts of the TPR profiles after methanol oxidation are listed in Table 1. A comparison of these values for the fresh and the used catalysts indicates that the samples containing higher amounts of K_2SO_4 were reduced to lower oxidation states.

X-Ray diffraction patterns of the used catalysts showed that other vanadium–potassium sulfate phases (*15*) were formed during methanol oxidation.

DISCUSSION

Figure 4 depicts the criteria selected to characterize the reaction and reduction behavior of the catalysts as a function of their K_2SO_4 content. The reducibility of the catalysts increases with the content of K_2SO_4. This indicates a weakening of the V=O bond due to the presence of the promoter. Addition of the first 20% K_2SO_4 lowers the temperature $T_{2.5}$ by 160 K. Further addition of K_2SO_4 has only a small effect on $T_{2.5}$. Consequently, the most drastic changes in oxygen-bond strength occur with catalysts A, B, and C having lower promoter contents.

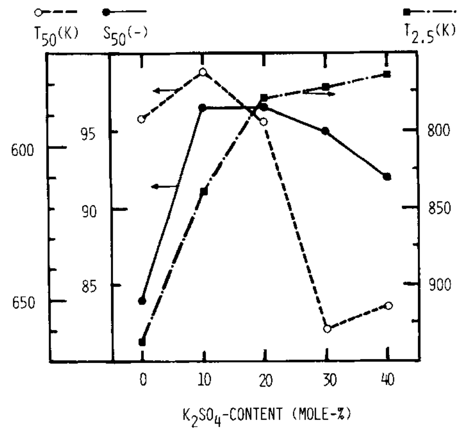

FIG. 4. Catalytic activity (T_{50}), selectivity (S_{50}), and reducibility ($T_{2.5}$) of the catalysts A to E as a function of their K_2SO_4 content. Definitions of T_{50} and S_{50} are given in Table 2. $T_{2.5}$ corresponds to temperature at which the loss of the weight due to reduction amounted to 2.5%.

The activity of the catalysts for methanol oxidation (curve T_{50}, Fig. 4) falls rapidly when the K_2SO_4 content exceeds 20%. The higher activity of catalyst B (10% K_2SO_4) as compared to pure V_2O_5 (catalyst A) is attributed to the larger BET surface area of this sample. The results shown in Fig. 3 indicate that addition of K_2SO_4 to V_2O_5 leads to a decrease of the activation energy of the methanol oxidation. This behavior may be explained by a change in the rate-determining step of the catalytic process. Weakening of the V=O bond can not only increase the rate constant of the reduction step of the reduction–oxidation mechanism, but also causes a decrease of the heat of reaction of the second step, i.e., the reoxidation of the catalyst surface. As a result of this, the reaction rate constant of the reoxidation step may be lowered to such an extent that the reoxidation becomes rate determining, and consequently the overall rate diminishes. The decrease in the valence of the vanadium ion after steady-state methanol oxidation with increasing promoter content (Table 1) supports this explanation.

Selectivity to formaldehyde is improved for all samples containing K_2SO_4. With pure V_2O_5, the maximum selectivity was 0.85; the promoted catalysts B and C exhibited a selectivity higher than 0.95. It should be noted that due to their low activity much higher temperatures had to be applied for the catalysts D and E to obtain a conversion of 0.5. This led to enhanced formation of the undesired total oxidation products CO and CO_2 and thereby lowered the selectivity to formaldehyde for these samples.

A comparison of the TPR profiles (Fig. 1) of the fresh catalysts with the profiles measured after methanol oxidation indicates that the temperature where reduction starts is lowered only for pure V_2O_5, whereas the opposite is true for the promoted catalysts. All samples characterized with TPR after methanol oxidation exhibited starting temperatures for the reduction of about 800 K.

The oxygen species reduced at temperatures lower than 800 K with the fresh catalysts were consumed before steady-state conditions were attained during methanol oxidation. The depletion of these oxygen species leads to lower amounts of V^{5+} in the catalysts with higher K_2SO_4 contents (Table 1).

It is generally assumed that catalysts having good reducibilities exhibit high catalytic activities but low selectivities for partial oxidation reactions. On the other hand, catalysts having low reducibilities show moderate activities but improved selectivities (*16*, *17*). The promoting action of K_2SO_4 on V_2O_5 catalysts for methanol oxidation is found to be an exception to this trend. Although the addition of K_2SO_4 leads to a lower bond strength of the oxygen in the mixed catalysts, the selectivity to formaldehyde is improved, whereas the activity decreases.

Electron microscope and X-ray diffraction results indicated that our catalysts B, C, and D are mixtures of well-developed plate-like V_2O_5 and the phase $5V_2O_5$ $3K_2SO_4$. The mixed phase formed agglomerates of small needle-type crystals. These findings are not in agreement with the behavior of the silica-supported V_2O_5–K_2SO_4 catalysts described by Sharma *et al.* (*5*) who observed the coexistence of V_2O_5 and K_2SO_4 without interaction. These different results may be ascribed to the fact that different catalyst preparation methods were applied. From the phase diagram given by Hähle and Meisel (13) it emerges that our catalysts were obtained from a V_2O_5–K_2SO_4 melt. The calcination temperature used by Sharma *et al.* (*5*) (550°C) was above the melting point of $5V_2O_5 \cdot 3K_2SO_4$ (505°C) but far below the melting point of V_2O_5 (690°C). It can therefore be excluded that the active phase on the silica support was obtained from a completely molten mixture of V_2O_5 and K_2SO_4.

CONCLUSIONS

In comparison with pure V_2O_5 the following modifications have been found to occur for unsupported mixed K_2SO_4–V_2O_5 catalysts:

(i) The oxygen-bond strength in the mixed catalysts is lowered if the K_2SO_4 content is increased from 0 to 40 mol%.

(ii) The activation energy for methanol oxidation decreases with increasing promoter content. The promoted catalysts exhibit a higher selectivity to formaldehyde in the whole temperature and composition range investigated.

(iii) The catalysts having lower oxygen-bond strengths are reduced to lower oxidation states during steady-state methanol oxidation.

(iv) The promoted catalysts are composed of two phases, pure V_2O_5 and $5V_2O_5 \cdot 3K_2SO_4$, with the latter phase consisting of agglomerates of needle-shaped crystals.

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