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Catalytic Activity of Vanadium Oxides in the Oxidation of Benzene

A. BIELAŃSKI, J. PIWOWARCZYK, AND J. POŹNICZEK

Faculty of Chemistry, Jagiellonian University, Karasia 3, 30-060 Kraków, Poland

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The catalytic oxidation of benzene over V_2O_5, V_6O_{13}, V_2O_4, V_7O_{13}, V_6O_{11}, V_5O_9, V_4O_7, V_3O_5, and V_2O_3 was investigated at 300–400°C. Stoichiometric V_2O_5 was catalytically inactive. However, after reduction with C_6H_6 vapor it became active and selective for formation of maleic anhydride. The catalyst was then an intimate mixture of V_2O_4, V_6O_{13} with smaller amounts of V_6O_{13} and V_4O_9. All the oxides lower than V_2O_5 were active without any pretreatment. The curve showing the initial catalytic activity versus average oxidation number of vanadium in particular oxides exhibited two distinct stronger and weaker maxima corresponding to V_2O_4 and V_4O_7 phases, respectively. In the course of the catalytic reaction the oxides lower than V_2O_4 were slowly oxidized and partially transformed into other phases. The most stable under the conditions of the catalytic reaction were V_2O_4 and V_6O_{13} in which vanadium practically did not change its oxidation state. The selectivity with respect to maleic anhydride in the case of the pure oxides was generally low and total degradation of benzene to carbon oxides and water predominated. However, the selectivity could be markedly improved by introducing MoO_3 into solid solution in V_6O_{13} or V_2O_4.

INTRODUCTION

Promoted and unpromoted vanadia catalysts are widely used for the oxidation of aromatic hydrocarbons. They are an example of catalysts whose chemical behavior and phase composition and hence also catalytic properties change as a function of the redox conditions of the surroundings. Simard *et al.* (*1*) stated the V_2O_5 was partially reduced to V_2O_4 and V_6O_{13} in the course of use as a catalyst in the oxidation of *o*-xylene. Bielański and Inglot (*2*) stated that the activity of V_2O_5 and V_2O_5–MoO_3 catalysts for the oxidation of benzene was highest when the average oxidation number of vanadium was close to IV. In all these cases the catalytically active mass may be composed of various oxidic phases. This fact arouses interest in the study of the catalytic properties of particular vanadium oxides lower than V_2O_5. Schaefer (*3*) investigated the oxidation of benzene on a series of VO_x samples with x equal to 1.94–2.50 and containing V_2O_5, V_6O_{13}, V_2O_4 or V_7O_{13} as single oxides or in a mixture and found the highest activity for V_2O_4. He also studied V_2O_3 but not the oxides of composition between V_7O_{13} and V_2O_3. According to Shaprinskaya *et al.* (*4*) the initial catalytic activity in the oxidation of naphthalene in the temperature range 380–415°C decreased in the sequence $V_6O_{13} > V_2O_3 > V_2O_4 > V_2O_5$, while Nishisaka *et al.* (*5*) found for the same reaction a quite different order, namely $V_2O_5 > V_6O_{13} > V_2O_4$. According to Colpaert (*6*), V_2O_5 was not active in the oxidation of propylene and V_6O_{13} was active and selective while V_2O_4 which exhibited the highest activity favored complete oxidation to carbon oxides. Andersson and Lundin (*7*) studied ammoxidation of 3-picoline over V_6O_{13}, V_2O_5, and V_2O_4 and stated that V_6O_{13} was the most selective and active, while V_2O_4 was inactive.

In the present investigation the catalytic properties of vanadium oxides were studied using benzene oxidation as the test reaction. A more complete set of vanadium oxides has been examined than was the case in previous investigations which concerned the oxides of the V_nO_{2n-1} series. Studies of transformations of the oxides under catalytic conditions were also undertaken in or-

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der to gain information concerning their stability.

Industrial catalysts for benzene oxidation always contain a certain amount of MoO_3 which in the fresh catalysts is contained mainly in the form of solid solution in V_2O_5. The presence of molybdena strongly enhances the selectivity to maleic anhydride. As the oxides studied by us were in most cases active but not selective catalysts we made an attempt to prepare the solid solutions of MoO_3 in V_2O_4 and V_6O_{13} phases and to compare their catalytic properties and especially their selectivity with those of undoped oxides. Only the solid solution of MoO_3 in V_2O_4 has been mentioned in the literature (*8*) but its catalytic properties were not investigated.

EXPERIMENTAL

The lower oxides of vanadium were obtained by sintering in evacuated and sealed quartz ampoules the appropriate mixtures of V_2O_5 or V_2O_4 with V_2O_3. V_2O_5 was analytical-grade "Reachim" preparation from which V_2O_3 was obtained by heating in a hydrogen stream for 4.5 h at 600 °C and subsequently for 4 h at 900°C. V_6O_{13} and V_2O_4 were synthesized by sintering the mixtures of V_2O_5 and V_2O_3 for 2–3 h at 550°C and then for 46 h at 650°C in the former case and for 20 h at 900°C in the latter. The oxides V_3O_5, V_4O_7, V_5O_9, V_6O_{11}, and V_7O_{13} were obtained by sintering the mixtures of V_2O_4 and V_2O_3 for 40 h at 800–900°C. Solid solutions of MoO_3 in V_2O_4 and V_6O_{13} were prepared similarly by sintering the mixtures of V_2O_5, V_2O_3, and MoO_3 in evacuated quartz ampoules. The amounts of oxides were chosen in such a way that the atom ratio of metal cations to oxide anions was equal to 2 : 4 or 6 : 13.

X-ray identification of the oxides was carried out using a DRON-1 X-ray diffractometer (USSR) and Cu*Kα* radiation. The X-ray diffraction patterns of the oxides were in agreement with the data given in ASTM Tables. In no case was contamination with other phases found. For the solid solutions V_nO_m–MoO_3, the rutile-type V_2O_4 or V_6O_{13} phases were identified as the sole phases thus showing that MoO_3 may form solid solutions not only with V_2O_5 but also with the other oxides of vanadium.

The mean oxidation number of vanadium was determined analytically as in Ref. (*2*). The results, which are given in Table 1, correspond well with the values calculated from chemical formulas.

Specific surface areas of the samples were determined by the BET method using adsorption of argon.

A constant flow microreactor containing 0.66 g of catalyst mixed with 5 g of ground quartz (grain diameter 0.25–0.4 mm) was used. A mixture of air with benzene vapor containing 9.3 mol of oxygen for 1 mol of benzene was flowed through the reactor with a velocity of 5.04 liters h^{-1}. The products of the reaction were collected in an absorber filled with glass beads covered with acetone kept at a constant temperature of −70°C. In the condensate the content of C_6H_6 was determined gas chromatographically and the maleic anhydride by titration with 0.05 *M* NaOH, the sample being diluted with water and boiled for 15 min.

In each experiment the fresh catalyst was heated from room temperature to 350°C in an atmosphere of oxygen-free nitrogen. The catalytic runs (30 min each) were repeated at this temperature for 5–6 h. In this time the samples reached a constant activity. Subsequently a series of measurements was carried out in which the dependence of the activity on the temperature (300–400°C) was followed. After the catalytic tests the grains of the catalysts were separated from ground silica under a binocular microscope and examined by X-ray diffraction. Their chemical composition was also determined.

RESULTS

With the sole exception of V_2O_5 all the vanadium oxides investigated were catalytically active without any pretreatment. Their activity and selectivity changed only slowly with the time. In most cases there

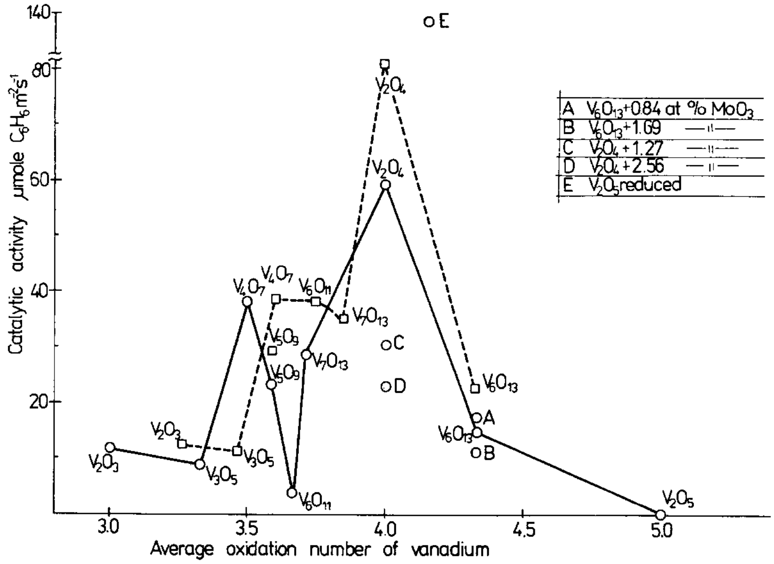

FIG. 1. Catalytic activity (conversion of benzene) of vanadium oxides determined at 350°C as the function of average oxidation number of vanadium. (—) Initial activity; (---) final activity.

were no changes observed during the initial 1.5 h of the experiment. The results obtained in the first 30-min run could thus be taken to be characteristic of fresh catalyst.

Fresh V_2O_5 was completely inactive at 350°C in accordance with our previous results (*2*). However, after a reduction carried out in a benzene vapor–air mixture at 450°C for 7 h it became much more active and selective than any other oxide.

The initial activity of the vanadium oxides expressed as the conversion of benzene under standard conditions (350°C) related to a surface area of 1 m^2 is given in Fig. 1 by a full line. Because of the small amount of the catalyst in the reactor it was not possible to determine its surface area after the catalytic experiments. For the sake of comparison we assumed to a first approximation that the surface area was not changed and we calculated the final activity by relating it to the surface area of the fresh catalyst. The results are shown by the broken line in Fig. 1. The results of X-ray investigation of the catalysts samples after use will be mentioned under Discussion.

The chemical compositions of the fresh and used catalyst samples are given in Table 1. The initial selectivity of the oxidation of benzene to maleic anhydride is given in Fig. 2.

DISCUSSION

The results show that stoichiometric V_2O_5 is a very poor catalyst for benzene oxidation at about 300–350°C but can be activated by an appropriate reduction. This is in accordance with our previous investigation (*2*) in which the dependence of activity and selectivity to maleic anhydride of V_2O_5 and V_2O_5–MoO_3 catalysts was studied as the function of catalyst reduction and, as already mentioned, the highest activity as obtained for samples in which roughly all V(V) was reduced to V(IV). In the present case it has also been shown that the reduced catalyst which was more active than any other simple vanadium oxide (Fig. 1) contained V_3O_7, V_4O_9, V_6O_{13}, and V_2O_4 but no V_2O_5 was present. Considering that its average composition corresponded to the formula $V_2O_{4.15}$ one can estimate that at least 55% of the vanadium was present in the form of V_2O_4 phase (on the basis that

TABLE 1

Average Oxidation Numbers of Vanadium in the Catalyst Samples

Sample	Phase identified by X-ray diffraction	Oxidation number of vanadium			Specific surface area of fresh catalyst ($m^2\ g^{-1}$)
		Theoretical value	Fresh catalyst	Catalyst after use	
1	V_2O_5	5.00	5.00	4.15	0.17
2	V_6O_{13}	4.33	4.32	4.33	0.29
3	V_2O_4	4.00	3.99	4.05	0.08
4	V_7O_{13}	3.71	3.70	3.85	0.29
5	V_6O_{11}	3.66	3.66	3.74	0.21
6	V_5O_9	3.60	3.59	3.59	0.24
7	V_4O_7	3.50	3.50	3.60	0.22
8	V_3O_5	3.33	3.33	3.47	0.83
9	V_2O_3	3.00	2.96	3.26	1.33

V_2O_4 and V_6O_{13} were the predominant phases). Very similar results were obtained by Shaprinskaya *et al.* (*4*) who studied the behavior of V_2O_5 catalyst in the oxidation of naphthalene to phthalic anhydride and found a very poor initial activity in pulse-type experiments. On the other hand, after a prolonged exposure of the catalyst to the reacting mixture of gases it became reduced and activated and in this state represented a complicated system containing in addition to V_2O_5 also V_6O_{13}, V_3O_7, and V_2O_4. These observations are the plausible explanation of the fact that Nishisaka *et al.* (*5*) have found the highest activity in this reaction in the case of V_2O_5 catalyst. Most probably they have been working with V_2O_5 samples which were reduced.

It should be observed here that Dziembaj (*9*) has shown that stoichiometric V_2O_5

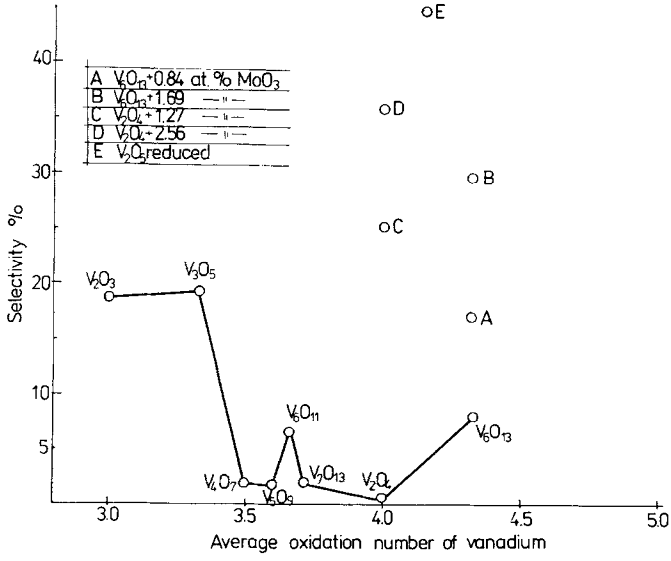

FIG. 2. Initial selectivity at 350°C of the catalytic oxidation of benzene to maleic anhydride as a function of average oxidation number of vanadium.

chemisorbs practically no oxygen. This is easy to understand as there are no donor centers which might supply the electrons necessary to form negatively charged oxygen surface species. The absence of chemisorbed oxygen must hinder the oxidation of benzene and may be a possible reason for the poor activity of stoichiometric V_2O_5 in the catalytic oxidation of benzene. The inactivity of such V_2O_5 catalysts also shows that the presence of doubly bonded oxygen $V{=}O$ on the (010) surface postulated by some authors to be active in the oxidation of hydrocarbons is not a sufficient condition for the oxidation of benzene. The necessity of the presence of vanadium in an oxidation state lower than (V) is evidenced by the fact that all lower oxides of vanadium exhibit catalytic activity in the oxidation of benzene without any pretreatment.

However, as the curves in Fig. 1 exhibiting two local maxima show, there is no simple relation between the average oxidation number of vanadium atoms in the oxides and their catalytic activity. Evidently the latter is influenced also by other factors, e.g., structural ones. V_2O_4, which is the most active of the investigated oxides, differs markedly in its rutile-type structure from the structure of V_6O_{13}. When nonstoichiometric (homogeneity range according to Ref. (*10*) between $VO_{1.995\pm0.002}$ and $VO_{2.002\pm0.002}$) with an excess of metal it must contain a certain concentration of statistically distributed defects involving V^{3+}, and when nonstoichiometric with an excess of oxygen it must contain a certain amount of defects involving V^{5+} ions. At any rate, V_2O_4 with its rutile-type structure and its deviations from strict stoichiometry must be considered the phase exhibiting high catalytic activity; this is proved not only by the present results but also by the previous investigation of Schaefer (*3*). It should also be observed that in Schaefer's investigation the highest activity was exhibited by the V_2O_4 phase with excess metal, the composition being $VO_{1.99}$. The activity of strictly stoichiometric VO_2 oxide was lower.

In the oxides lower than V_2O_4 which constitute a homologous Magnéli type series V_nO_{2n-1}, the layers of rutile-type structure are separated by crystallographic shear (CS) planes parallel to the (121) plane and their crystal structures change monotonically from V_8O_{15} to V_3O_5 by a gradual decrease in the distance between the CS planes. No discontinuity in the values of magnetic moment [11] or in the α-emission bands of vanadium (*12*) was observed and the appearance of a maximum in initial catalytic activity for V_4O_7 samples was rather unexpected. In the search for an explanation of this fact the following hypothetical model may be proposed. Let us first observe that in the oxides belonging to the V_nO_{2n-1} homologous series, ordering of V^{4+} and V^{3+} must take place. Both are situated in $[VO_6]$ octahedra, the former in the layer of rutile structure in which each corner is shared by three octahedra, resulting in a cation : anion ratio equal to 1 : 2, and the latter in the octahedra participating in the CS defect in which corner oxygen atoms are shared in such a way that the cation : anion ratio becomes 2 : 3. One can expect that rutile layers are now stoichiometric and less active than the nonstoichiometric V_2O_4 phase. This would be a plausible explanation of the decrease in activity observed in the case of V_7O_{13} and V_6O_{11} samples in which domains of rutile structure are relatively large. However, some new factors must appear enhancing catalytic activity, the roles of which become more and more important as the value of n in V_nO_{2n-1} formula decreases. It is logical to assume that this factor is in some way associated with the presence of CS planes. In particular the appearance of an activity maximum at V_4O_7 would be easy to understand if the assumption were made that in the homologous series of oxides active centers also exist which involve two $[VO_6]$ octahedra, one of them containing a V^{4+} ion and belonging to the rutile layer and the other containing a V^{3+} ion and belonging to the CS defect zone. The concentration of such catalytic centers would increase with the increasing density of CS planes. It would reach a maximum in the case of V_4O_7 in which the numbers of octahedra of both kinds are equal. In V_3O_5 the number of such double octahedron centers must again decrease because the $V^{3+} : V^{4+}$ atom ratio is no longer equal to 1 : 1.

According to the data given in Table 1 all oxides lower than V_2O_4 (with the exception of V_5O_9) were somewhat oxidized in the course of the catalytic reaction. This also resulted in the appearance of new X-ray diffraction lines corresponding to phases more oxidized than the predominant initial one. The most strongly transformed catalyst was V_2O_3 in the case in which X-ray analysis also revealed the presence of V_7O_{13} and even small amounts of V_2O_4. The samples most stable under the conditions of catalytic reaction at 350°C were V_2O_4 and V_6O_{13}. The oxidation number of vanadium in the former increased only by 0.06 and the X-ray diagram indicated that in addition to the initial monoclinic modification a small amount of some other phase, possibly the triclinic modification of V_2O_4 observed by Mitsuishi (*13*), was present. It should be observed here that between 64 and 72°C the monoclinic (distorted rutile) structure transforms into the tetragonal modification with undistorted rutile structure and which is stable under the catalytic conditions (*14*). V_6O_{13} practically did not change its composition but in the X-ray diagram a new unidentified line appeared. The high stability of V_6O_{13} with respect to its transformation in V_2O_4 was noted previously by Dziembaj *et al.* who observed that above 400°C V_2O_5 decomposed reversibly into V_6O_{13} (*15, 16*); however, the decomposition of V_6O_{13} to V_2O_4 did not occur *in vacuo* at the same temperature and heating to about 650°C was necessary to initiate this process (*17*). The unexpected stability of V_5O_9 which suffered no oxidation and in which no formation of any other vanadium oxide could be detected might be associated with the presence of incidental impurities, because in addition to its own 12 diffraction lines 5 unidentified weak lines appeared in the X-ray diagram taken after the catalytic experiments.

Despite the changes in the chemical and phase composition of the samples the essential features of the curve showing their final activity to be a function of chemical composition are similar to those of fresh samples. The broken curve in Fig. 1 exhibits two maxima, for V_2O_4 and V_4O_7, although the latter is much less distinct.

The selectivity pattern of single-phase undoped vanadium oxide catalysts shown in Fig. 2 is rather complicated. In no case is the selectivity to maleic anhydride high. For V_5O_9 and V_7O_{13} it does not exceed 2.5%. The samples with higher selectivity, namely V_2O_3 and V_3O_5 (nearly 20%) as well as V_6O_{11} and V_6O_{13} (about 7%), are those with lowest specific activity. Hence in the case of single-phase undoped vanadium oxides roughly speaking the selectivity increases with a decrease in activity. However, this is not the case with the reduced V_2O_5 catalyst which is simultaneously highly active and selective. These properties may be in some way associated with the presence of interfaces between the different phases remaining in intimate contact.

Interesting results were obtained with the samples of V_2O_4 and V_6O_{13} doped with MoO_3. As Figs. 1 and 2 show, doping diminished the activity but quite markedly increased the selectivity in quantitative accordance with the trends observed with single-phase undoped vanadium oxides. The effect of MoO_3 additives increasing the selectivity of V_2O_5-based catalysts is well known, but the present results show that the enhancement of the selectivity is not associated with any particular phase.

Let us now note that the oxidation of benzene has been shown by many authors (*18, 19*) to occur by two parallel processes, viz. (i) direct degradation of benzene to carbon oxides, and (ii) oxidation to maleic anhydride. There is also a process (iii) whereby maleic anhydride may suffer degradation to carbon oxides. Selectivity is high if reactions (i) and (iii) are slow in comparison to (ii). The enhancement of selectivity by doping vanadium oxides with MoO_3 must in some way block the centers on which total oxidation occurs and (or) activate the centers of selective benzene oxidation. The facts that doping V_2O_5 with MoO_3 results in distinct retention of the rate of catalyst reduction (*20*) suggests that the presence of molybdenum causes an increase in the oxygen bonding strength and this is a probable reason for the improved selectivity.

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