Temperature-Programmed Reduction Studies of V-Ag Catalysts

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In H_2/N_2 atmosphere, the reduction behavior of V-Ag catalysts with V/Ag atomic ratios 1/0, 9/1, 3/1, 2.16/1, 1.5/1, 1/1, and 0/1 were studied by temperature-programmed reduction (TPR), X-ray diffraction (XRD), and ultraviolet diffuse reflectance spectra (UVDRS). The results showed that the reduction processes of $Ag_2V_4O_{11}$, $Ag_2V_4O_{10.84}$, and $Ag_{1.2}V_3O_8$ are all the same while the reduction temperature was raised; they were first reduced to Ag and V_6O_{13}, then to VO_2, and thence to V_2O_3 subsequently. To vanadium oxides in V-Ag catalysts, the reactions with hydrogen were accelerated and the peak temperatures (T_M) of TPR were decreased explicitly due to the addition of silver element. © 1998 Academic Press

INTRODUCTION

Vanadic oxide is one of the main components in the catalysts for the selective oxidation reactions. In general, as the other metal elements are added to the vanadic oxide, various mesophases and solid solutions, such as the ortho-vanadate ($3M_2O \cdot V_2O_5$), the pyrovanadate ($2M_2O \cdot V_2O_5$), the metavanadate ($M_2O \cdot V_2O_5$), and the vanadium bronze ($M_x \cdot V_2O_5$), are formed, which result in some changes for the bond strengths of vanadium-oxygen, the transfer capacity of oxygen in the bulk phase, the transfer velocity of the charges in catalytic reactions, and the acid/base properties on the surface in these compounds. Consequently their catalytic capacity can be changed. In Ref. (1) the catalytic activities of vanadic oxide with silver added for the selective oxidation of toluene to benzaldehyde have been described. The results showed that after adding the elemental silver to vanadic oxide, the bond strength of V=O was weakened (1), the activation energy values of desorption of surface oxygen species decreased explicitly (2), and during the reaction, the silver-vanadium oxide phases formed ($Ag_xV_2O_5$ ($x = 0.80$ and 0.68)) were responsible for the selective oxidation of toluene. In this paper, these oxides were studied by temperature-programmed reduction (TPR); furthermore, the X-ray diffraction (XRD) and ultraviolet diffuse reflectance spectra

(UVDRS) were used to perform the analysis for the V/Ag = 2.16 sample after TPR determination. The purpose was to recognize the reduction properties of vanadium-silver oxides and to correlate the results obtained with the catalytic activities of the selective oxidation reaction of toluene.

EXPERIMENTAL

1. Sample preparation. In the light of a certain proportion of vanadium and silver desired, 200 ml silver nitrate aqueous solution was added to 200 ml ammonium meta-vanadate aqueous solution (in which a small amount of oxalic acid (about a mole ratio 1/12 of $H_2C_2O_4/NH_4VO_3$) was also added to promote dissolution) with constant stirring. The suspended mixture formed in the liquid was placed in a circulating film-evaporator to evaporate. The dried mass was calcined in a muffle furnace at 450°C for 9 h, and then these materials were pelleted, crushed, and sieved.

2. Specific surface area measurements. The specific surface area of BET was measured with the aid of ASAP 2000 type porosity/specific surface instrument. Helium was used as the carrier gas, the adsorbate was nitrogen, and the measurements were carried out at the liquid nitrogen temperature.

3. TPR measurement. The TPR apparatus used in this work is similar to that described in Ref. (3). The measurements were performed in U-shaped quartz tube ($\varnothing$ 3 mm) using a N_2-H_2 (5.5% H_2) gas mixture with purity of 99.999% flowing at 20 mL/min. The sample amount was 20 mg. The heating rate was 10 K/min. The T_M values for TPR are the peak temperatures which were measured from TPR profiles. The amount of hydrogen consumed for each peak in the TPR profile was determined from the TPR peak area with a normalization method, so a percentage can be given for each of these peaks in the TPR profiles. For Sample 4 (V/Ag = 2.16), in order to determine the fractional reduction product, an *in-situ* quartz cell was adopted as described in Ref. (4). First, according to the experimental conditions required by the XRD and UVDRS, the

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integrated TPR profile was drawn; next, for each peak on the TPR pattern the temperature was increased to the peak temperature and maintained until the peak was completed. Then, the sample was cooled in N_2-H_2 stream to ambient temperature. During the XRD and UVDRS measurements, the reduced sample could be reoxidized if it was exposed to the air; therefore, in order to avoid being oxidized, these reduced samples were covered with a film of polystyrene (5).

4. XRD analysis and UVDRS measurement. After each TPR peak was completed, the reduced sample was covered with the polystrene film. Then the XRD analysis and the UVDRS measurement were carried out in ambient atmosphere, respectively. The XRD was performed with a Rigaku D/Max-RA X-ray diffractometer, using a Cu target and a graphite monochrometer, with an applied voltage of 40 kV and a current of 150 mA, respectively. The UVDRS was recorded on a ultra-violet-diffuse reflectance spectrometer of UV-2100 type, using wave lengths of 190–700 nm. $BaSO_4$ was used as the reference compound.

RESULTS AND DISCUSSION

The TPR spectra are shown in Fig. 1. The constituent, the specific surface area, and the T_M of a series of V-Ag-O catalysts with different V/Ag atomic ratios are given in Table 1. For the TPR spectrum of Sample 1 (pure V_2O_5), there are three reduction peaks (Fig. 1.1), the T_M values for the peaks are 688, 724, and 848°C in turn, and the ratio of each peak area to the total area is 32%, 17%, and 51%, respectively. Hence, a value of 2:1:3, i.e. a proportion of the consumed amount of hydrogen in the three reduction stages, can be obtained. According to the report of Bosch (6), the reduction of vanadic oxide is reduced from V_2O_5 to V_6O_{13} to V_2O_4 to V_2O_3. Apparently, for such a reduced process in TPR, the amount of vanadium does not change. The reduction process for V_2O_5 can also be written as: $3 \cdot V_2O_5 \rightarrow V_6O_{13} \rightarrow 3 \cdot V_2O_4 \rightarrow 3 \cdot V_2O_3$. Thus in this process, the changes of the oxygen amounts could be expressed as: $2 \cdot O \rightarrow 1 \cdot O \rightarrow 3 \cdot O$. This is consistent with the ratio of the consumed amounts of hydrogen in the three reduction stages, i.e. in the three reduced peaks in the TPR experiment for V_2O_5. So, the reduction process of V_2O_5 in TPR can be described as follows: $V_2O_5 \rightarrow V_6O_{13} \rightarrow V_2O_4 \rightarrow V_2O_3$.

The TPR profile of Sample 7, which was prepared from the silver nitrate through thermal decomposition in the air, appeared only as a horizonal straight line without any peaks (see Fig. 1.7). However, as the elemental silver is added to the V_2O_5 sample, the profile of TPR and T_M values apparently changed, which indicated that the reduction process of composite oxides is more complex than the simple ones. Meanwhile, Ref. (2) had reported that in the V-Ag-O sample the activation energy value (Ed) of the desorption of surface oxygen species (O^- and O^{2-}) de-
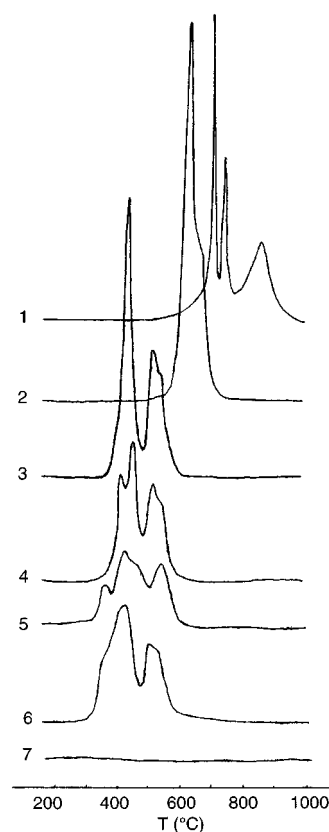

FIG. 1. TPR profiles of V-Ag samples prepared. The numerals (1–7) are the numeral order of the samples, respectively (see Table 1).

creased obviously; therefore, this could explain the decrease of T_M values of TPR of the V-Ag-O catalysts in Fig. 1.

For selective oxidation of toluene to benzaldehyde, the research results of vanadium–silver catalysts showed that the selectivity of benzaldehyde of V_2O_5 or Ag is very low; it is only 6.1% or 0.0%, respectively (1). But, while silver was added to V_2O_5 the catalytic activity exhibited an obvious enhancement. For example, the selectivity of benzaldehyde of Sample 4 (V/Ag = 2.16), as compared with the other

TABLE 1
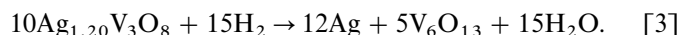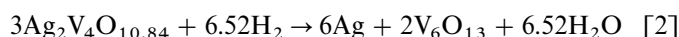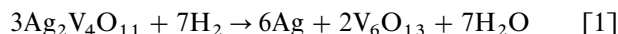**Constituent, Specific Surface Area, and T_M of Different V-Ag Samples**

| Sample	V/Ag atomic ratios	Specific surface area (m²/g)	T_M (°C)
1	1/0	4.07	688,724,848
2	9/1	3.95	610,650(sh)[a]
3	3/1	1.78	423,500,524(sh)[a]
4	2.16/1	1.13	400,435,500,525(sh)[a]
5	1.5/1	0.82	345,406,450,520
6	1/1	0.59	340(sh),410,494
7	0/1	0.20	—

[a]Sh: shoulder peak

V-Ag samples, was the best and arrived at a high level of 57.0%. Besides, the selectivity of the other products for Sample 4 is as follows: benzoic acid, $\sim 20\%$; CO_x, 17%; and the remainder, a small amount of moleic anhydride. Hence, in this paper, we selected to measure the TPR and to analyse the phases formed and the changes in valence states of these two metal elements during TPR processes.

The results of the phase analyses of XRD showed that during the preparative process for vanadic oxide a redox reaction occurred due to the addition of silver. Thus, part of the V^{5+} were reduced to V^{4+}, vacancies of the oxygen ions were formed, and these conditions made it very complex for the phase constituents of the V-Ag-O system. For Sample 4, the XRD pattern (Fig. 2a) showed that it contained vandium bronze phases, $Ag_2V_4O_{11}$, $Ag_2V_4O_{10.8}$, and $Ag_{1.20}V_3O_8$, but the phases of vanadium oxide are not found. Therefore, the existing valence states of silver and vanadium in Sample 4 should be $+1$ and $+4$ and $+5$, respectively, which is consistent with the analytic results of IR and ESR, described before (1).

From Fig. 1.4, it can be seen that the TPR profile of Sample 4 consists of three reduction peaks, the T_M are 400, 435, and 500°C, respectively, and at 525°C a shoulder peak appears. In the H_2/N_2 atmosphere, while the temperature was raised to 400°C, i.e. at the first peak of TPR, the analysis of XRD (Fig. 2b) showed that, due to the reductive reaction, we obtained the vanadium bronze phases, $Ag_2V_4O_{11}$, $Ag_2V_4O_{10.84}$, and the $Ag_{1.20}V_3O_8$ vanished, the silver formed, and the diffraction peaks of V_6O_{13}, VO_2, and V_2O_3 appeared, the silver with $+1$ valence state and the vanadium with $+5$ valence state are not found; meanwhile, the strengths of diffraction peaks of V_6O_{13}, VO_2 are rather weak. Such results, perhaps, are the reason that the TPR reduction process is accompanied by the calcination process in the elevated temperature, so the solid solution of V_6O_{13} and VO_2 with Ag are formed (7). Based on the above-mentioned circumstances, the reduction reactions in this reduction process can be expressed as

$$3Ag_2V_4O_{11} + 7H_2 \rightarrow 6Ag + 2V_6O_{13} + 7H_2O \quad [1]$$

$$3Ag_2V_4O_{10.84} + 6.52H_2 \rightarrow 6Ag + 2V_6O_{13} + 6.52H_2O \quad [2]$$

$$10Ag_{1.20}V_3O_8 + 15H_2 \rightarrow 12Ag + 5V_6O_{13} + 15H_2O. \quad [3]$$

Then, a part of V_6O_{13} is reduced; two sequential reductions

$$V_6O_{13} + H_2 \rightarrow 6VO_2 + H_2O \quad [4]$$

and

$$2VO_2 + H_2 \rightarrow V_2O_3 + H_2O. \quad [5]$$
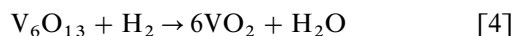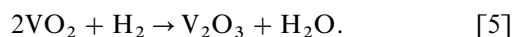
occur, consequently.

FIG. 2. XRD patterns of Sample 4 (V/Ag = 2.16) at different stages of TPR with H_2/N_2: (a) before reduction; (b) first TPR peak; (c) second TPR peak; (d) third TPR peak; (e) after shoulder peak of TPR. In patterns, the symbols used for the phases and the numbers of JCPDS cards are as follows: I—$Ag_2V_4O_{11}$, 20-1385; O—$Ag_2V_4O_{11-y}$, 20-1386; Δ—$Ag_{1.20}V_3O_8$, 23-647; #—Ag, 4-0783; +—VO_2, 31-1439; ϕ—V_2O_3, 34-187; X—V_6O_{13}, 27-1318.

Analysis of the XRD of the second reduction peak at 435°C (Fig. 2c) showed that although a large quanity of silver exists, the diffraction peaks of V_6O_{13} disappeared. Moreover, the strengths of the diffraction peaks of VO_2 were also decreased and nearly approached zero. In comparison with the first reduction peak, the strengths of the diffraction peaks of V_2O_3 were higher. This demonstrated that the V_6O_{13} and VO_2 in the solid solution state had been reduced deeply.

According to the XRD analysis of the third peak at 500°C (Fig. 2d), it can be seen that the diffraction peaks of VO_2 vanished, but the diffraction peaks of V_2O_3 became very strong. This result indicated that a large quantity of VO_2 in the solid solution state were reduced. In this elevated temperature circumstance the formed V_2O_3 aggregated, and it did not combine with silver to form the solid solution. However, the vanadium compound in a lower valence state could not be found.

As the reduction temperature was raised to 525°C, a shoulder peak appeared; the XRD analysis indicated that only two phases of Ag and V_2O_3 existed (Fig. 2e) and the strengths of these diffraction peaks are very strong. In the meantime, vanadium compounds in lower valence states are not found. These results showed that in the general condition of reduction the higher valence states of vanadium in the oxide can merely by reduced to $+3$ valence, which coincides with the results of Ref. (6).

The UVDRS of sample 4 after stepwise reduction are given in Fig. 3. From Fig. 3a it can be seen that the absorption peaks of the unreduced sample appeared at a wave length of 220–290 nm. In general, these peaks should be attributed to the contribution of transition of $^1S_0(4d^{10}) \rightarrow {}^1D_2(4d^95S^1)$ of Ag^+ (8). The absorption peak at 400 nm is referred to the characteristic absorption of V^{5+} posited in the octahedral environment. The absorption peak at about 600 nm, however, could be assigned to the contribution of the d-d transition of V^{4+} in the distorted octahedral symmetric environment (9). Therefore, it can be proposed that in this sample the silver with $+1$ valence and the vanadium with $+4$ and $+5$ valences are contained; XRD analyses also give similar results. The result of the

UVDRS (Fig. 3b) indicated that the absorption peak of Ag^+ vanished and the absorption peak at 310 nm caused by the electron transition of $^1D_2(4d^95S^1) \rightarrow {}^2P_{1/2}(4d^{10}5P^1)$ of the silver atom appeared. Moreover, the characteristic absorption peak of V^{5+} did not vanish completely and the featured absorption peak of V^{4+} still existed. Apparently, the Ag^+ ions have been reduced to the silver element and the V^{5+} ions began being reduced to lower valence states. For the UVDRS of the second reduction peak (Fig. 3c), the characteristic absorption peak of V^{5+} had disappeared completely; besides the featured absorption peak of the silver atom, the featured absorption peak of V^{4+} still existed. At the third reductive peak, according to Fig. 3d, only the featured absorption peak of silver atom was found and that of V^{4+} did not exist; the reason may be that the surface V^{4+} had been reduced at such a high temperature. The same phenomenon is also found in the IR measurements of molybdena systems reduced at a high temperature due to the surface M_O^{6+} having been reduced, so the absorption peak of the IR cannot be found (10). After the reduced temperature is raised further (Fig. 3e), the featured absorption peak of the silver atom existed, while the characteristic absorption peak of $+4$ and $+5$ valence vanadium ions disappeared, too. Combine this result with the analysis of XRD and it is clear that V^{4+} was reduced to V^{3+}.

To sum up, in H_2/N_2 atmosphere the reduction stages of the vanadium and silver in Sample 4 are: first, $Ag^+ \rightarrow Ag$ and $V^{5+} \rightarrow V^{5+}$, V^{4+}, respectively; then, V^{5+}, $V^{4+} \rightarrow V^{4+}$; and at last, $V^{4+} \rightarrow V^{3+}$.

TPR is one of the effective methods used to characterize the solid metal oxide (11). But, in TPR measurement, in order for correct results of measurement and good profiles of TPR to be obtained, the choice of raising the temperature rate is important. Generally speaking, in a relative low temperature-raising rate, for example, less than 2 K/min, and in an oxygen-free condition, the oxygen lost from the oxide sample influenced the reduction process. However, in this experiment due to the temperature-raising rate, 10 K/min average, the rate for the oxide reduced by hydrogen is far greater than the oxygen loss rate, so that the latter influence should be neglected. Therefore, except for the TPR measurement, the other method, for example the thermogravimetry, is not needed in the reduction measurement for this oxide sample. For the TPR measure it was said that the special reduction temperatures of the pure metal oxides can be used to characterize their properties. If the other components were added to the one metal oxide and the T_M values of each component were constant, without any change in the TPR, this would indicate that the metal oxides had not reacted with each other. Otherwise, the formation of some composite oxides or some solid solution would inevitably lead to the change of the T_M values. Therefore, the oxide systems which formed by blending different kinds of metal elements in various proportions could exhibit a special
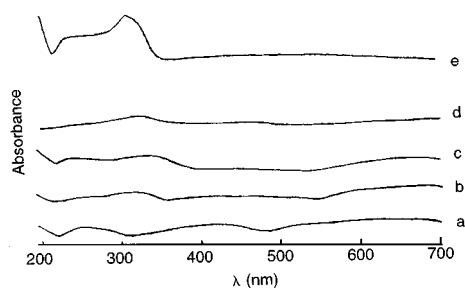

FIG 3. UVDRS of Sample 4 (V/Ag = 2.16): (a) before reduction; (b)–(e) after reduction, the first peak to the shoulder peak of TPR, respectively.

redox property and be applied to some selective oxidation of hydrocarbon. According to the transformation of the reduction temperatures of the V-Ag oxide system mentioned above, it showed that an interaction occurred between the two metal oxides, which would promote the dispersion of V_6O_{13} and VO_2 since vanadium bronze compounds were formed during preparation and the solid solution was formed in the TPR process that followed. Thus, these results led to the apparent decrease of the desorption active energies of the surface oxygen species. The reduction of these samples is becoming facile and their T_M values largely descend. Consequently, at an appropriate ratio of V/Ag components (for example, the sample with a ratio of V/Ag = 2.16), because the reduction capacity is moderate (characterized by the T_M values of the first reduction peak of the TPR in Table 1), the catalytic activity for the selective oxidation of toluene to benzaldehyde is better.

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