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Propylene Oxidation on $TeO_2 \cdot SiO_2$ Catalysts

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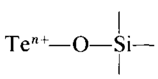
Interaction of orthotelluric acid with a silica support in the temperature range between 500 and 700°C leads to the formation of oxotellurosilica surface complexes with Te(IV) in a regular tetrahedral coordination and to free paratellurite. The performance of the catalysts is correlated to these two distinct active Te(IV) species, varying in concentration depending upon the formal composition. In the low TeO_2 region ($< 10\%$ TeO_2) where tetrahedral Te(IV) prevails, products of cracking, typical of the pure support, are largely suppressed by the surface



$$Te^{n+}\text{—O—}\overset{|}{\underset{|}{Si}}\text{—}$$

complexes; selectivity to acrolein is low and catalytic activity decays rapidly. The allylic oxidation process, leading to acrolein, is favored over the TeO_2-rich catalysts containing the strongly distorted octahedral sites of free paratellurite. The distinct catalytic performances are related to different redox capacities of the two Te(IV) species.

INTRODUCTION

An interesting theme of research in catalysis by metal oxides is the study of the interaction of the carrier and supported metal ions: in particular it appears of interest to discover whether the symmetry of the host oxide is modified by the support and to define correlations between catalytic activity and induced changes in coordination geometry, bond strengths, valence state, etc. The problem appears of sufficient generality to demand thorough investigation.

The present paper attempts to give an answer to these problems for the particular case of TeO_2 as catalyst in the oxidation of propylene. The interest in this field is demonstrated by the fact that until lately numerous research studies and patents have appeared on TeO_2 as the principal catalytic element or promoter (*1–6*). The most striking property of such TeO_2-based catalysts is the high selectivity to acrolein, especially in case of a silica support. To provide a satisfactory interpretation of the catalytic activity, extensive studies have been carried out in our laboratory on the solid state properties of these catalysts. We have investigated (a) the nature of the phases in the TeO_2–SiO_2 system as a function of the concentration, temperature and silica type (*7*), (b) the thermal degradation of pure orthotelluric acid (*8*), and (c) the effects of the support on the decomposition of H_6TeO_6 (*9*). Marked structural differences were shown by means of various chemical-physical techniques. Most notable at the lowest TeO_2 compositions is the presence of an unknown absorption band at 260 nm as opposed to the 310 nm band characteristic of pure TeO_2. This observation was taken as a valid argument to study effects of interaction with the support and eventual changes in valence state and/or coordination of tellurium, in rela-

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tion to the catalytic oxidation of propylene to acrolein.

EXPERIMENTAL METHODS

Preparation of the Catalysts

Samples containing 2 to 15 wt% TeO_2 were prepared by impregnation of microspheroidal commercial silica (Davison) with an aqueous solution of H_6TeO_6 (Schuchardt). After drying overnight at 110°C, the catalysts were calcined at 480°C for 4 hr in a fluid bed in an air-water vapor flow [~3:1(v/v)] or at 700°C in an oven for 4 to 32 hr. The samples containing 47 wt% TeO_2 were prepared by coprecipitation of solutions of H_6TeO_6 and 30% SiO_2 gel (Ludox), followed by drying and activation.

Physicochemical Characterization

Surface areas accessible to N_2 at −196°C were determined by means of the BET method. (Cross-sectional area of adsorbed N_2 was taken as 15.4 Å^2.)

Infrared spectra were recorded with a Perkin–Elmer spectrometer Model 225 using standard quantities of the samples in Kel–F suspension. Ultraviolet and visible reflectance spectra were obtained with a Perkin–Elmer Hitachi EPS-3T spectrometer in the range 210–700 nm using MgO as a reference.

Catalytic Activity

The catalytic oxidation of propylene was studied by making use of a flow-microreactor equipped with capillary flowmeters. To improve the precision of dosage, excess amounts of gas components (air:propylene = 12:1) were mixed, out of which 3.3 liters/hr were fed into the microreactor containing 0.25–2 ml of catalyst (150–270 mesh), at variable contact times ($\tau = 0.12$–1 sec) calculated at the reaction conditions. The experiments were carried out at 440°C and at a total pressure of 920 Torr. Products were analyzed gas chromatographically as described elsewhere (*10*), and the carbon content of used catalysts was determined by microanalytical techniques.

RESULTS

Figure 1 illustrates the variation of surface areas with composition and calcination conditions. Samples pretreated at 480°C display an almost linear variation with the TeO_2 content, whereas a sharp drop is observed between 6 and 8 wt% TeO_2, after calcination at 700°C. In both cases surface areas are significantly lower than those expected from the contribution of the support only, indicating a strong chemical and physical interaction between the components, in accordance with previous observations (*7–9*). This is particularly evident if we consider that (i) sintering of SiO_2 in the presence of steam occurs only appreciably at $T > 600$°C, thus at a much higher temperature than used in our experiment, (ii) sintering of SiO_2 in dry air occurs only at $T > 700$°C, as shown previously (*11*).

Electronic spectra of catalysts pretreated at 480°C are characterized by strong absorption in the 240–320 nm range (Figs. 2 and 3). Distinctive features in the low TeO_2 region are: (i) the position of the maximum, which shifts with composition from 250 to 265 mm (<10 wt% TeO_2), leveling off afterwards; (ii) the intensity, which is maximum around the 6–10 wt% TeO_2. Tellurium-richer samples display a strong absorption band at ~300–315 nm; this absorption starts as a shoulder at lower TeO_2 contents and increases with composition until it becomes prominent as in the 47 wt% sample (Fig. 2, curve C). Reflectance spectra of the samples of the 700°C series (Fig. 3) indicate, in agreement with results of surface areas, profound structural differences between the TeO_2-poor (<8 wt%) and TeO_2-richer (>10–15 wt%) catalysts. In particular we notice a shift of the absorption band around 250 nm towards higher wavelengths for the samples up to 4 wt% TeO_2; the maximum occurs in fact at 260 nm and the band intensity is greater than in the 480°C series. In the 10–15 wt% range, the 305 nm band intensity strongly decreases; the TeO_2-rich region is thus characterized by crystallization of TeO_2 and cristobalization effects (*7*).

Infrared spectra of samples calcined at 480°C, recorded in a range (5000–1500 cm^{-1}) free of absorption due to TeO_2 (*7*), show three intense absorption bands at 3650, 3400 and 1615 cm^{-1}, the first of which is attributable to OH groups, the others to H_2O (*12,13*). The intensity of the 3650 cm^{-1} absorption band diminishes towards higher tellurium contents (Table 1), in a nonlinear fashion with the surface areas, thus suggesting increasing interaction of TeO_2 with the Si–OH groups.

Results of catalytic activity are given in Fig. 4 for the 480°C series; for the sake of clarity only the values recorded at reaction temperature $T = 440°C$ and contact time $\tau = 1$ sec are reported here, whereas those associated with different experimental parameters (T and τ), are collected in the

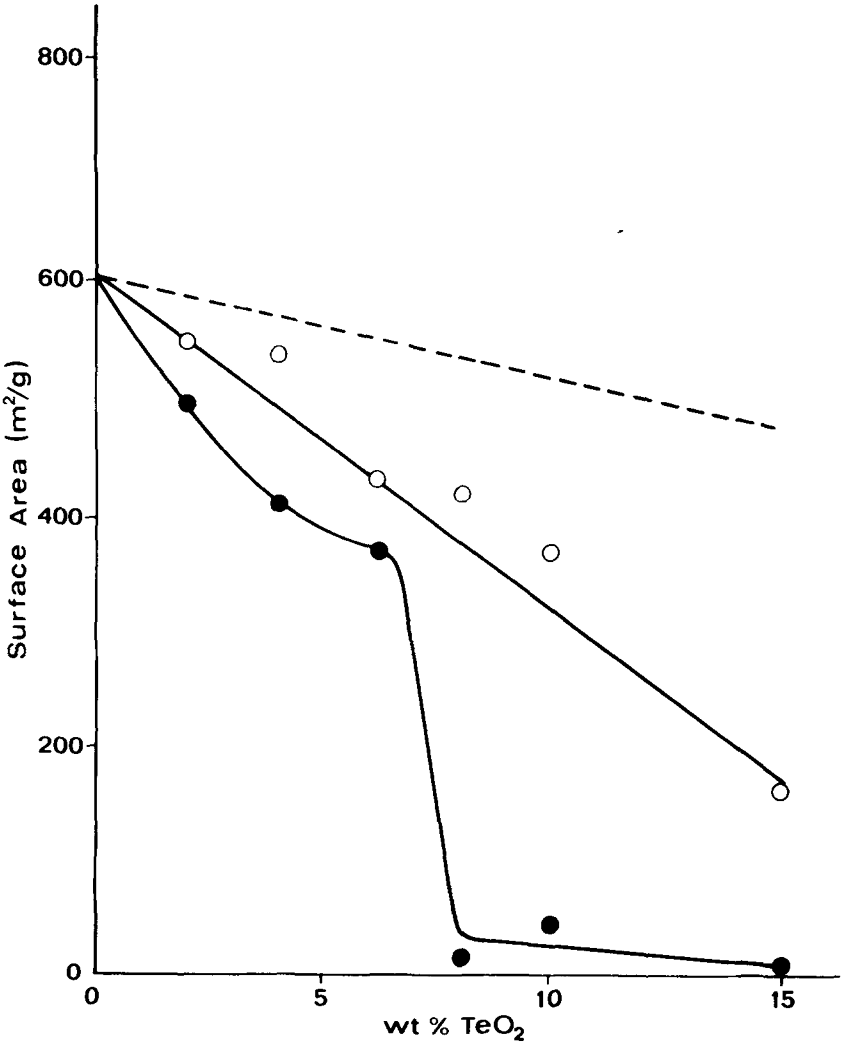

FIG. 1. Variation of surface areas of $TeO_2 \cdot SiO_2$ catalysts with composition and calcination conditions: (○) 4 hr at 480°C in air–vapor mixture; (●) 4 hr at 700°C in air; (--) the calculated contribution of the support.

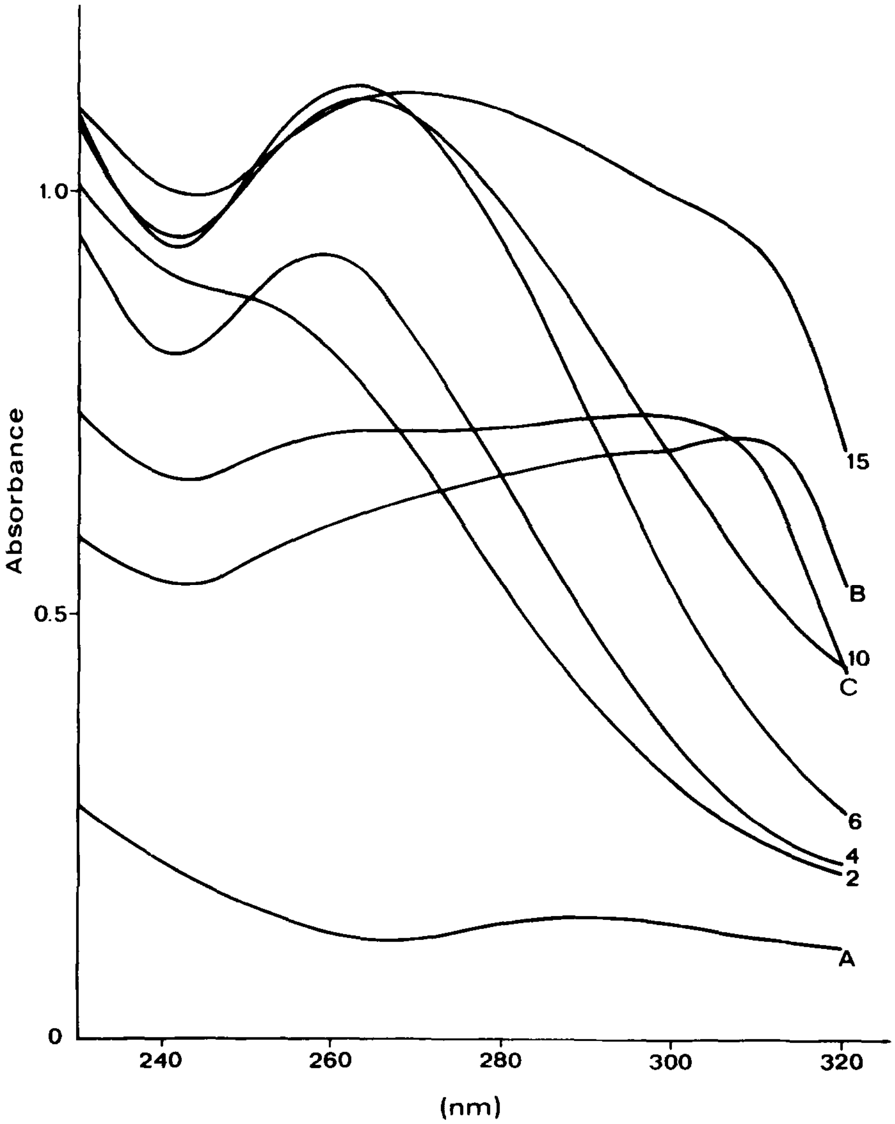

FIG. 2. Ultraviolet reflectance spectra of $TeO_2 \cdot SiO_2$ catalysts. (A) Silica gel; (B) TeO_2 after calcination at 600°C for 4 hr; (C) 47 wt% $TeO_2 \cdot SiO_2$ sample after 8 hr at 500°C and 60 hr at 600°C. Other curves refer to catalysts containing the indicated amount of TeO_2 (wt%), after calcination at 480°C for 4 hr.

plots of Fig. 6. All values are those read at the end of a 4 hr experiment (end-point values), occasionally after a slight decay in catalytic activity due to aging (see below), although steady conditions were always attained before the end of the experiment. More specifically, the conversion of propylene increases with the TeO_2 content until it reaches a maximum at about 8 wt% TeO_2; then it decreases, probably on account of lower surface areas (Fig. 1). The latter assumption is proven by the observation that if end-point conversions are referred to unit-weight TeO_2, values thus calculated vary almost linearly, obeying the same dependence with surface areas in the whole range of compositions (Table 1). Additional information relevant to catalytic activity is collected in Table 1. A discontinuity at 8–10 wt% TeO_2 is evident in

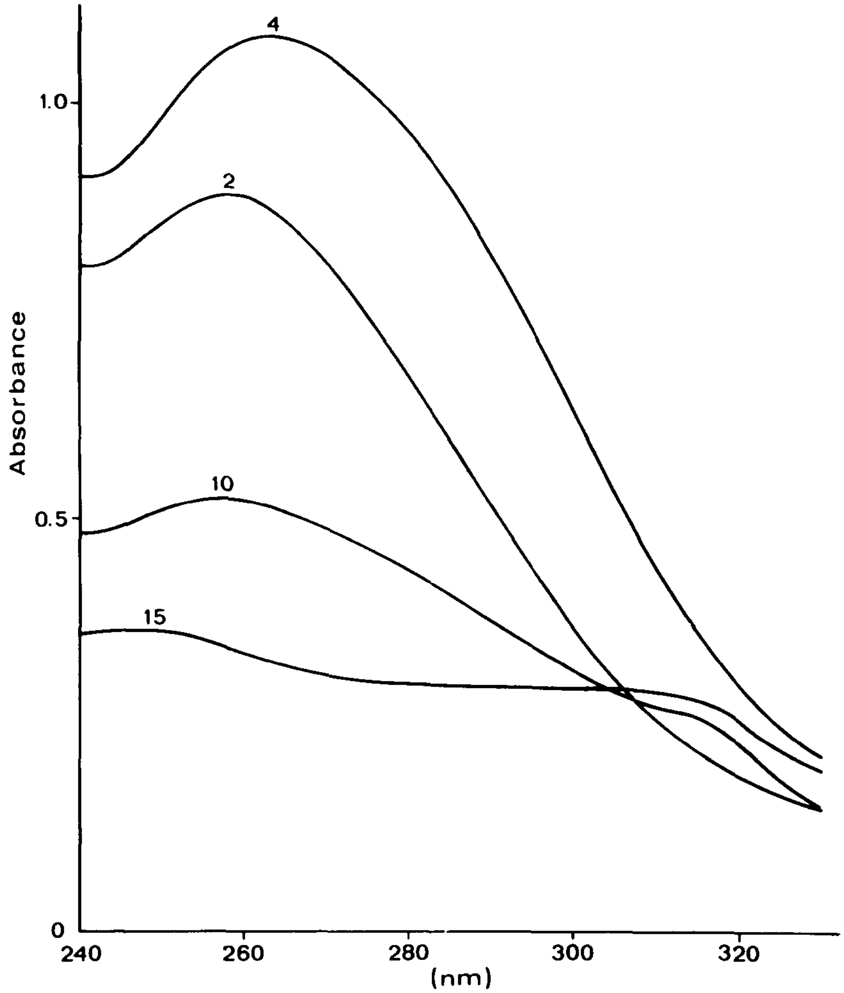

FIG. 3. Ultraviolet reflectance spectra of $TeO_2 \cdot SiO_2$ catalysts after calcination at 700°C for 4 hr, containing varying amounts of TeO_2, as indicated in wt%.

the intensity of the 3650 cm^{-1} band in fresh catalysts; note also for spent catalysts the absorption at ~500 nm, attributable either to cracking phenomena or to the presence of metallic tellurium (*14*), and the percentage of carbon chemisorbed by the solid. All these quantities decrease gradually on going from SiO_2 to the 8–10 wt% TeO_2 sample, leveling off at their lowest values at higher compositions. Catalytic activity also suffers a discontinuity, as indicated by the fractional decay of conversion which exhibits a sharp maximum at 4 wt% TeO_2, decreasing to zero at about 15 wt% TeO_2 for $\tau = 1$ sec (Table 1). For lower contact time the decay is more pronounced.

As to the selectivities, acrolein, acetaldehyde and CO_x account for the observed conversion, as no other by-products could be detected among those specifically sought (*10*). Main features are: (i) increase of acrolein with the TeO_2 concentration, as opposed to the trend of acetaldehyde and CO_x; acetaldehyde is not formed beyond 6 wt% TeO_2 (Fig. 4); (ii) slight variations of the selectivities with aging, being most pronounced in the lowest TeO_2 region, with a tendency for acrolein to decrease and for acetaldehyde

TABLE 1

Sample wt% TeO$_2$	% Conv. × 10^{2} [a] / g TeO$_2$	SA (m^2/g)[b]		A_{3650}[c] (cm^{-1})	A_{500}[d] (nm)	% C by microanalysis[e]	ΔC Conversion decay[f] (%); τ (sec):		
		Initial	Final				1.00	0.50	0.25
0	—	620		0,244	1,4	1,06	Nil		
2	17.5	561	585	0,252	1,1	0,70	14.4	18.5	26.6
4	11.5	549	547	0,143	0,8	0,35	17.2	27.0	28.2
6	8.9	439		0,125	0,5	0,16	12.9		
8	7.7	420		0,137	0,3	0,03	12.3		
10	5.6	375		0,102	0,2	0,09	9.3		20.6
15	3.3	185		0,098	0,2	0,06	Nil	11.6	15.1
47	0.8	39			0,2	0,04	Nil		

[a] End-point conversion relative to runs with $\tau = 1$ sec.

[b] Surface areas of used catalysts after runs with $\tau = 1$ sec.

[c] Intensity of the 3650 cm^{-1} ir absorption band of fresh catalysts; the variation due to SiO$_2$ content is neglected.

[d] Intensity of the 500 nm absorbance (taken from value of plateau between 400 and 700 nm) for spent catalysts at $\tau = 1$ sec.

[e] Carbon microanalysis of spent catalysts at $\tau = 1$ sec.

[f] Percentage fractional decay of conversion calculated from the first (*i*) and end-point conversion (*f*) as [conv (*i*) − conv (*f*)]/conv (*i*) × 100.

to increase with time on stream. Examples of this behavior are illustrated in Fig. 5, for runs at $\tau = 0.25$ sec. With the 700°C series (calcination time 32 hr), catalytic activity was observed only in case of the 2 and 4 wt% samples, giving conversions of 22 and 4%, respectively, under the same standard conditions as in Fig. 4 ($T = 440°C$ and $\tau = 1$ sec). Selectivities to various products vary similarly with the 480°C series. The degree of fractional decay of catalytic activity and the accompanying variations of selectivities are greater than in the 480°C series, showing that sintering strongly affects the catalytic performance.

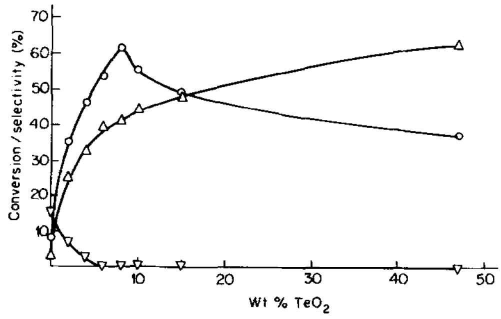

FIG. 4. Conversion of propylene (○), expressed as sum of product yields and selectivities to acrolein (△) and acetaldehyde (▽) over TeO$_2$·SiO$_2$ catalysts. Experimental conditions: $T = 440°C$, $\tau = 1$ sec, propylene:air ratio = 1:12.

To quantify the effects of composition and structural changes, results on samples activated at various temperatures and tested under conditions different from the reference (Fig. 4) have been arranged in Fig. 6 in terms of the end-point conversions vs selectivities to acrolein and acetaldehyde. The comparison clearly depicts some characteristic features of the system, which can be summarized as follows: (i) at any conversion level, increased TeO$_2$ content leads to higher selectivities to acrolein, as opposed to the behavior of acetaldehyde; (ii) acrolein and acetaldehyde always decrease with increasing conversion, causing formation of CO$_x$; (iii) both the selectivities to acrolein and to acetaldehyde tend toward maximum values as conversions are extrapolated to zero, thus indicating that they are both primary reaction products.

To gain further insight into the catalytic reactivity, spent catalysts were examined by optical reflectance spectroscopy after

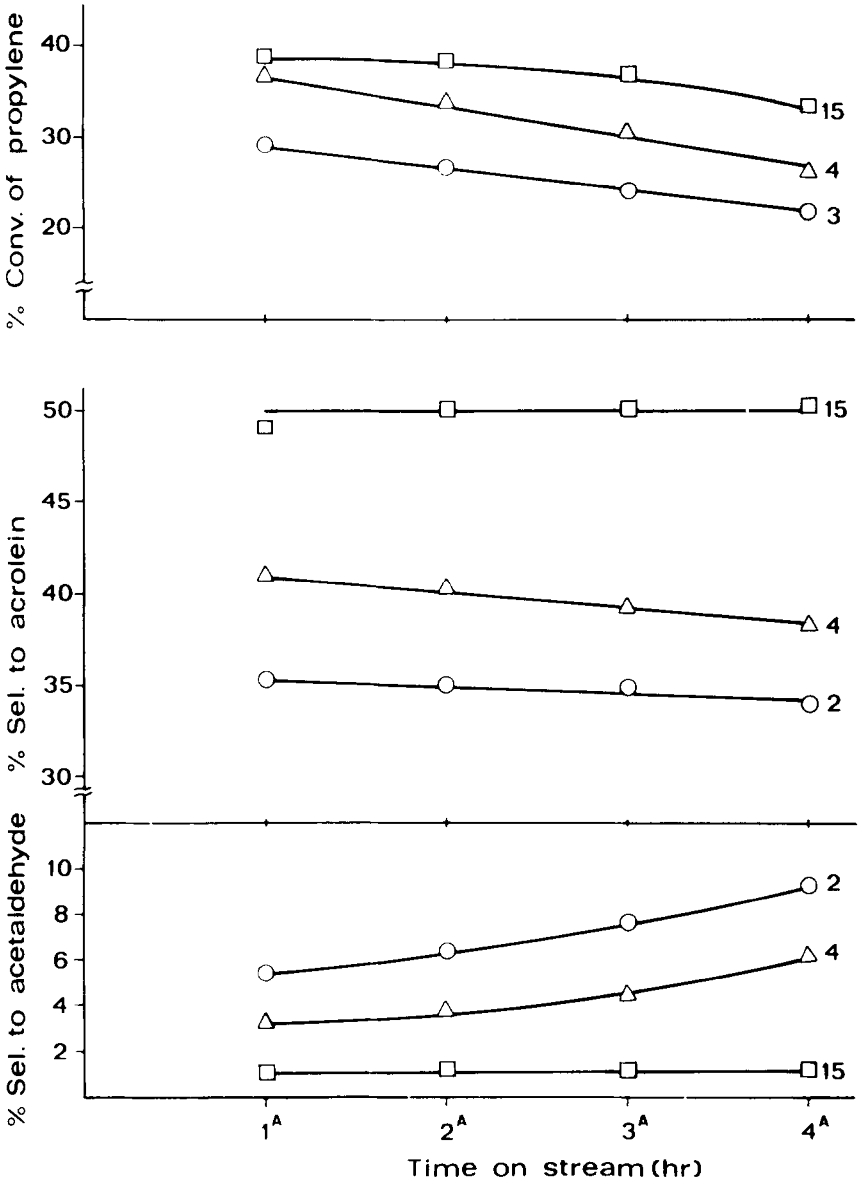

FIG. 5. Influence of time on stream on conversion of propylene and selectivities to acrolein and acetaldehyde for runs at 440°C; $\tau = 0.25$ sec, using TeO_2·SiO_2 catalysts (480°C series) containing the indicated wt% TeO_2.

reoxidation in air. With reference to a typical sample (Fig. 7), we notice that characteristics of the original spectra are only partly restored as the band intensity of the spectra is lower; on the other hand, the continuous absorption in the visible region of spent samples persists, indicating eventually the presence of metallic tellurium not reoxidizable under the given conditions.

To evaluate further the performance of Te(IV)-based catalysts, some catalytic experiments have been performed on samples containing Te(VI) (9), namely 10 wt% TeO_2 on γ-Al_2O_3 (activated at 500°C) and one consisting of TeO_2, NaOH and

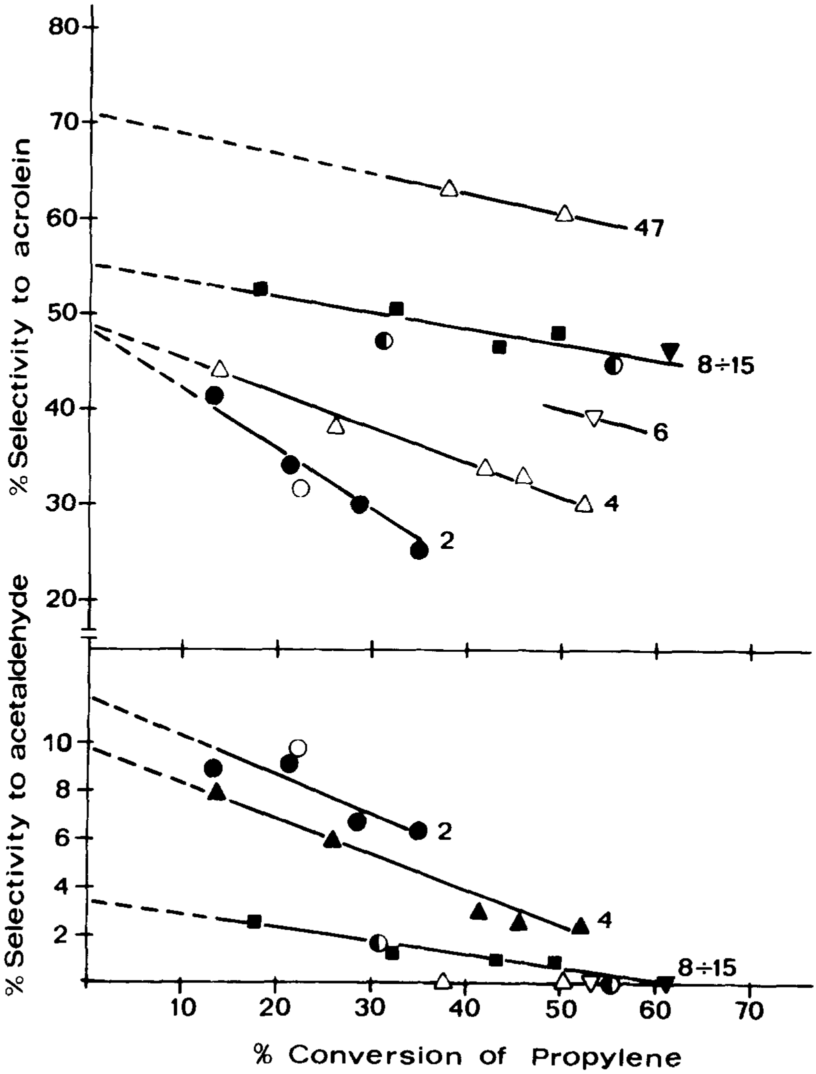

FIG. 6. Conversion vs selectivity to acrolein and acetaldehyde (end-point values) for runs at τ from 0.13 to 1.0 sec, T = 440°C, using $TeO_2 \cdot SiO_2$ catalysts of the 480°C series.

SiO_2 (Ludox) in the molar ratio 1:1:10. Under standard conditions, conversions were, respectively, 44 and 5%; products were exclusively CO and CO_2.

DISCUSSION

In discussing the nature of active species in the TeO_2–SiO_2 system, let us consider first the cracking activity, which shows a discontinuity at about 10 wt% TeO_2. As it has been demonstrated (*15*) that surface "free" OH groups of silica gel tend to interact with propylene and acrolein to form rather stable complexes and polymeric species, we interpret the cracking phenomena (Table 1) observed for the unloaded silica support and for catalysts containing low tellurium contents as being due to an analogous action of hydroxyl groups. Indeed, cracking diminishes with decreasing OH contents (Table 1), thus suggesting increasing formation of

$$Te^{n+}\text{—O—}\overset{|}{\underset{|}{Si}}\text{—}$$

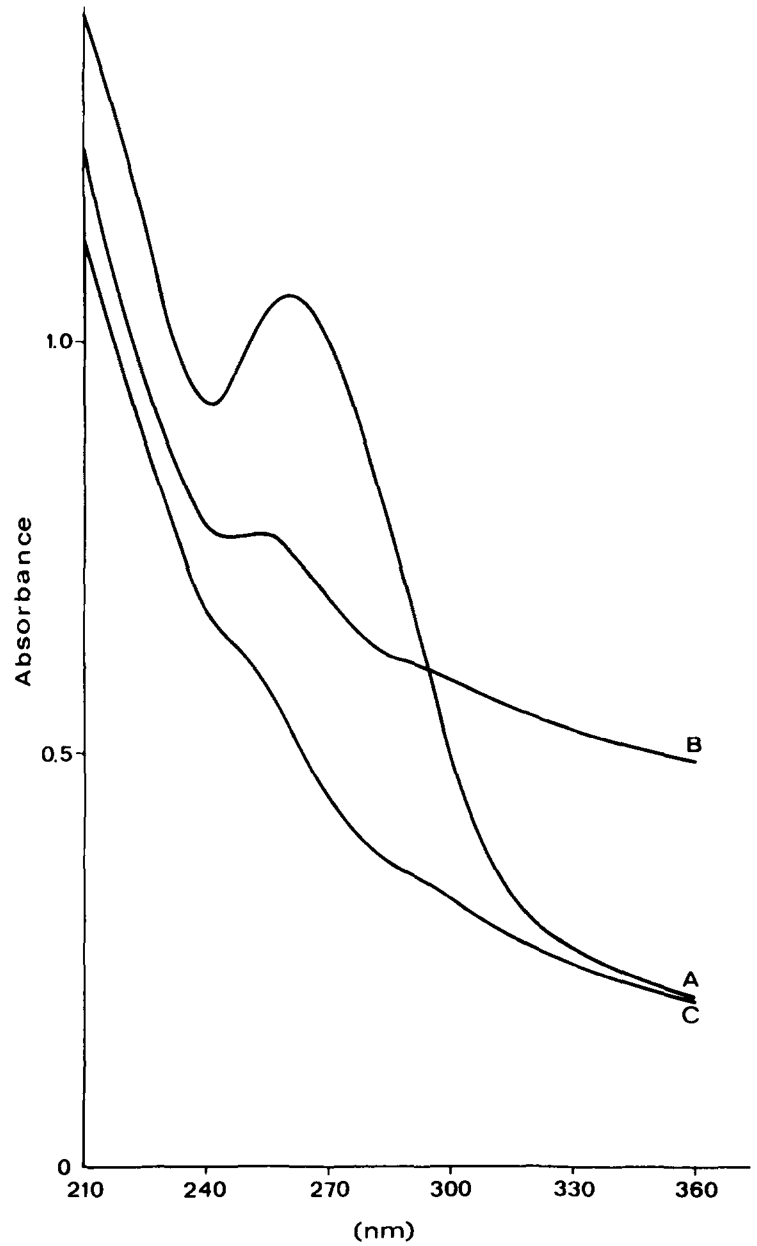

FIG. 7. Ultraviolet reflectance spectra of 2 wt% $TeO_2 \cdot SiO_2$ activated at 700°C for 32 hr. (A) Original sample; (B) after reaction; (C) as in (A) but reoxidized in air at 500°C for 2 hr.

surface sites. This feature is essentially the same as that proposed by Anderson (*13*) for various oxides supported on silica and also it does not appear to be conceptually different from that applying to many other catalytic systems differing in the nature of the oxide and the support itself. Moreover, the observation of an abrupt change in catalytic performance beyond the 10 wt% TeO_2 composition suggests that different Te-oxo species are also present. The observation is consistent with spectroscopic evidence which indicate a 310 nm band at higher TeO_2 contents as against the 260 nm absorption of the low-TeO_2 compositions. Two catalytically active functions thus appear to be present: at low concentrations, there is tellurium bound to the support via interaction with the OH groups and absorbing at 260 nm, while in tellurium-rich catalysts there is free TeO_2 (310 nm).

As to the nature of the (Te, Si)O complexes, the reactive sites of the support are defined generically as the free Si-OH groups, thus without making any statement about their concentration and precise identity. In fact, identification in terms of the A- or B-sites of Armistead *et al.* (*16*) is made difficult in case of the first series of catalysts by lack of knowledge on the equilibrium concentration of OH groups in the presence of steam [Ref. (*16*) refers to treatment of SiO_2 *in vacuo*]. In case of the second series of experiments, calculations show that a residual content of H_2O at 700°C in the order of 3.2% corresponds to a surface coverage of about 25%, requiring 12 wt% TeO_2 for complete reaction, on the assumption of interaction of the OH groups and TeO_2 in a 1:1 ratio. At the same time, it is possible that the 3650 cm^{-1} band may be due in part to Te–OH groups.

No direct information is available in the literature on other aspects of the (Te, Si)O complex: on account of the preparative route of the catalysts, it may be suggested that interaction of telluric acid with silica forms complexes containing the Te^{6+} ion as a $[TeO_4]^{2-}$ group, which is generally agreed to be more stable than the pure acid. Tellurates absorb around 260 nm (cf. K_2TeO_4), in accordance with data of Earley *et al.* (*17*) and Scott and Leonard (*18*), who observed a continuous shift in absorption from 230 nm towards higher wavelengths during gradual neutralization of a H_6TeO_6 solution with NaOH. Nevertheless, the hypothesis of Te(VI)-containing complexes, stable in our experimental conditions, appears highly improbable on the basis of the following observations: (i) TG analysis of $TeO_2 \cdot SiO_2$ catalysts indicate that the decomposition of telluric acid (dehydration and depletion of oxygen) is almost complete at 500°C (*9*); (ii) no variations in uv absorption spectra of tellurium-poor catalysts are observed even after drastic thermal treatment, as, e.g., in case of the 2 wt% TeO_2 sample after 50 hr at 850°C (if the 260 nm band were to be attributed to a fraction of H_6TeO_6 stabilized as such by the support, this would not explain the persistence of the absorption band at this high temperature); (iii) the uv spectrum of a sample prepared by activation at 500°C (8 hr) in inert atmosphere from a mechanical mixture of TeO_2 and SiO_2 does not show the characteristic absorption of free TeO_2 (310 nm) but exhibits instead the 260 nm band.

To evaluate further the nature of the 260 nm band, we draw attention to the behavior of tellurium in a chlorine environment (*19–21*), where two absorption bands at 270–290 and 360–380 nm vary in intensity depending upon the acid concentration and the nature of ligands. As $Cl^- > O^{2-}$ in the spectrochemical series, there appears to be an analogy between the 270–290 nm of tetrahedral $TeCl_4$ (*19–21*) and the 260 nm band in our samples; the latter is thus attributed to Te(IV) in tetrahedral oxygen coordination. This assignment can be rationalized by considering the structure of bulk TeO_2 (paratellurite), consisting of strongly deformed octahedra with four nearest oxygen atoms at Te–O distances of 1.91 to 2.09 Å (*22–24*) and two more weakly bonded oxygens at 2.89 Å, leading to a 4 + 2 coordination number. The effect of the support may thus be related to weakening of these latter oxygens and formation of isolated Te–O tetrahedra at reactive sites (in correspondence with the surface OH groups), in accordance with the ir spectra (Table 1); other oxy compounds are also possible, as suggested in previous work (*7*) and by the strong departure of surface areas from linearity (Fig. 1). Both the surface and bulk compounds formed thus have essentially a tetrahedral coordination; at higher TeO_2 concentrations, bulk TeO_2 (paratellurite) prevails, giving rise to the 310 nm band which is related to the pseudo-octahedral tellurium coordination.

Altogether the system appears to provide a good example of catalytic activity governed by the coordination of the host ion and not complicated by effects of varying valence state, i.e., absence of Te(VI). In cases where Te(VI) is present, experimental evidence indicates very strong preference toward total oxidation such that its role as a selective catalyst can be ruled out. Te(IV) thus appears the only selective species: within these limits we must distinguish the tetrahedral structures characterized by lower selectivities to acrolein (Fig. 6) and some decay of catalytic activity with time (Fig. 5). However, as decay and cracking display a different dependence upon the composition (Table 1) the former thus seems not entirely related to the concentration of OH groups of the silica. Other sources of reduced activity may be sintering and reduction, but as surface areas of used catalysts were found to be the same or even higher than those of the fresh samples, reduction is more likely to be responsible. This is also confirmed by the following observations: (i) the absorption band at 260 nm decreases in intensity in used catalysts, indicating fewer active species (Fig. 7); (ii) the persistence of the absorption in the visible region, denoting metallic tellurium even after reoxidation (Fig. 7); (iii) the decay of catalytic activity with surface areas which is greater on the most sintered samples (compare the 700 and 480°C series). Altogether, one may interpret the observed behavior as indicative of low reoxidizability of the tetrahedral Te(IV) surface structures, probably due to the absence of more weakly bound oxygens. The possibility that the decline in catalytic activity might be ascribed to losses of volatile Te compounds or metallic Te was not further considered, as full reoxidation of used catalysts restores almost completely the catalytic activity; thus, any effect related to the loss of active components is masked by the influence of surface reduction. The interpretation given for the decay of catalytic activity agrees rather well with the effects of aging, namely decrease of acrolein and increase of acetaldehyde with time: this behavior may be explained by progressive depletion of oxygen and to increasing formation of Te(0), this causing a corresponding alteration of the allylic oxidation vs side reactions, as in fact observed. Quite a similar explanation has been advanced for the $MoO_3 \cdot SiO_2$ system (*25*) following the observation that acetaldehyde formation is closely dependent upon the presence of reduced molybdenum species.

Observations pertaining to the tetrahedral region are further supported by results on the higher TeO_2 region. Main features here are the enhanced stability to aging (Fig. 5) and higher selectivities to acrolein (Fig. 6), comparable to those found over pure TeO_2. The only by-product present (CO_x) appears to arise mostly from a parallel reaction, as demonstrated by the fact that it reaches values of the order of 30% when selectivities are extrapolated to zero conversion.

CONCLUSIONS

The catalytic properties of the $TeO_2 \cdot SiO_2$ system (2–47 wt% TeO_2), prepared by thermal decomposition of orthotelluric acid at $T > 500°C$, can be described on the basis of two active sites, namely surface bound tellurium in a regular tetrahedral oxygen coordination and bulk paratellurite. Formation of acetaldehyde and CO_x prevails on the tetrahedral sites as opposed to the allylic oxidation process favored on the pseudo-octahedral sites. On account of the observed high selectivity, the latter thus appears suitable for allylic oxidation of olefins, as already reported for other binary systems. Decay of catalytic activity, most pronounced in the tetrahedral region, leads to the view that catalytic activity is associated with the weakly bound oxygens in bulk TeO_2 which should therefore participate in the redox mechanism.

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