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Structure and Activity of Tellurium–Cerium Oxide Acrylonitrile Catalysts

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Ammoxidation of propylene to acrylonitrile (ACN) was investigated over various silica-supported (Te,Ce)O catalysts at 360 and 440°C. The binary oxide system used consists of a single nonstoichiometric fluorite-type phase α-(Ce,Te)O_2 up to about 80 mole% TeO_2 and a tellurium-saturated solid solution β-(Ce,Te)O_2 together with α-TeO_2 at higher tellurium concentrations. The ACN yield varies almost linearly with the tellurium content of (Ce,Te)O_2. The β-(Ce,Te)O_2 phase is the most active component of the system (propylene conversion and ACN selectivity at 440°C of 76.7 and 74%, respectively) and is slightly more selective to ACN than α-TeO_2. Tellurium reduces the overoxidation properties of cerium and selective oxidation occurs through Te(IV)-bonded oxygen.

INTRODUCTION

As is well known, TeO_2 may act as an oxidation catalyst, converting ethylene to acetaldehyde (*1, 2*) or propylene to acrolein (*3*). Even more important is its application in combination with MoO_3. Recently it has been shown that although the TeO_2–MoO_3 system has highly desirable oxidation properties (*4*) and is superior to other TeO_2-based binary systems (*5*) its performance can be improved by a function balancing its redox properties. Cerium performs such a function and leads to an efficient acrylonitrile (ACN) catalyst, the properties of which will be described in a forthcoming paper (*6*). In our attempts to describe the structure and catalytic properties in selective oxidation of hydrocarbons of this commercially available ammoxidation catalyst on a (Ce,Mo,Te)O basis (*7*) we have recently paid attention to the (Te,Ce)O subsystem. As reported before, the latter combination is suitable both for the conversion of butenes to butadiene (*8*) and for the ammoxidation of propylene to ACN (*9, 10*). Its usefulness for the purpose of oxidation of (un)saturated hydrocarbons is illustrated by the fact that some 30 patents were filed in the decade 1962–1972 claiming ammoxidation catalysts based on both oxides, eventually in combination with others. Amongst the latter, the most interesting systems are the Nitto (Ce,Sb,Te)O catalyst and the aforementioned Montedison (Ce, Mo,Te)O catalyst (*7, 11*).

The present paper describes some aspects of the catalytic performance of the (Te,Ce)O system in the ammoxidation of propylene in relation to our current knowledge of the solid-state properties of the system (*12*).

EXPERIMENTAL

Preparation of the catalysts. Typical results of the catalytic experiments reported below refer to catalysts prepared according to a standard procedure and tested under equal operating conditions. Preparation of catalysts containing 25 wt% active phase was carried out by contacting the support (microspheroidal silica, Ketjen) with proper acidic solutions (nitric acid, 65%) of compounds of the desired components: $Ce(NO_3)_3 \cdot 6H_2O$ (Treibacher, 99.9%) and H_6TeO_6 (Schuchardt, 98.5%).

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The experimental procedure was such as to allow formation of stable solutions of the salts over the full composition range, thus avoiding precipitation. The volume of the combined solution was taken equal to the pore volume of the silica to be impregnated. In the absence of a carrier, preparations of unsupported catalysts followed the same route. Catalysts were allowed to stand overnight, then dried for 4 h at 110°C, and finally heated 8 h at 500°C, in air. Reference to the catalyst composition is made as molar percentages of the components TeO_2 and CeO_2.

Testing of catalytic performance. Catalytic activity was determined in a combined downflow fixed-bed microreactor and gas-chromatographic unit (Fractovap model C, Carlo Erba). The stainless-steel reactor (i.d., 1 cm; length, 10 cm), provided with an axial thermocouple well, was heated in a coaxial oven.

Catalysts were tested under the following standard conditions (flow experiments): catalyst volume, 4.5 ml; feed (molar ratio $C_3H_6 : NH_3 : \text{air}$), 1 : 1 : 10 using propylene of 98–99% purity; contact time τ, 2.5 sec; temperature, 400–440–460°C; pressure, 1 atm. The results reported below refer to $T = 440°C$ only, but in spite of this limitation they are representative of the catalytic behaviour. While under these circumstances it is obviously not possible to establish optimum performance of each catalyst, a relative ordering of the activities can be assessed which is useful for the sake of comparison.

The premixed feed gases were metered to the reactor by means of flow control devices. The condensable and noncondensable reaction products were analyzed by standard gas-chromatographic techniques (*4*).

Similarly, a series of experiments of depletive oxidation was performed by the slug technique by injecting pulses of C_3H_6 and NH_3 in a stream of the carrier gas (N_2) flowing through the catalyst bed held at 360°C.

Throughout this study conversion (C) and selectivities (S_i) are defined as follows:

$$C = \frac{\text{wt } C_3^- \text{ fed} - \text{wt } C_3^- \text{recovered}}{\text{wt } C_3^- \text{fed}} \cdot 100\%,$$

$$S_i = \frac{\text{wt } C_3^- \text{converted to product } i}{\text{wt } C_3^- \text{ fed} - \text{wt } C_3^- \text{recovered}} \cdot 100\%.$$

Catalyst characterisation. BET surface areas were measured using N_2 as the adsorbate. Pore volumes and pore size distribution were determined by means of mercury porosimeter Carlo Erba Models AG60 and 70H for the 1000- and 2000-atm ranges, respectively.

Phase analysis of fresh supported catalysts was performed by X-ray diffraction with Ni-filtered Cu$K\alpha$ radiation (λ = 1.54178 Å) using a calibrated Philips goniometer.

RESULTS

Catalytic Activity

Pulse experiments, which show the effect of progressive depletion of lattice oxygen by repeatedly passing slugs of propylene–ammonia over supported (Te,Ce)O catalysts under standard conditions at 360°C, indicate that the component oxides and their interaction products differ strongly in ammoxidation activity both with regard to conversion of propylene and the product distribution. In general terms, CeO_2 is essentially an overoxidation catalyst; its main products are CO and CO_2, and no ACN is formed. The binary compositions (Te,Ce)O and TeO_2 are considerably more active. TeO_2 is most selective to ACN and produces fair amounts of acrolein together with CO and CO_2; the ACN fraction increases with the degree of reduction of the catalyst, whereas selectivity to acrolein decreases (cf. Fig. 4 in Ref. (*4*)).

Figure 1 shows the catalytic oxidation performance of the SiO_2-supported binary system TeO_2–CeO_2 at 440°C under flow conditions as a function of the composition;

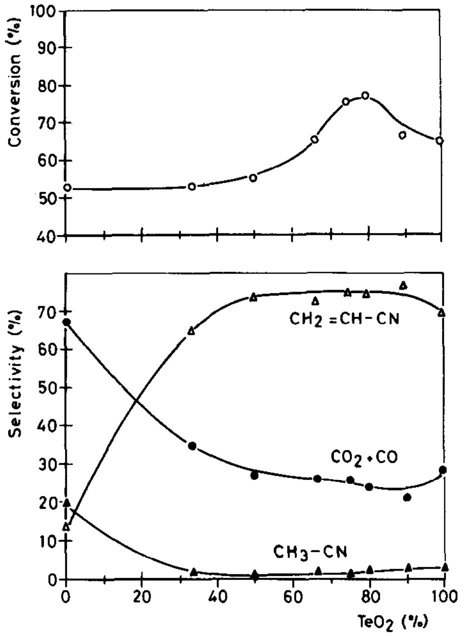

FIG. 1. Catalytic activity of SiO_2-supported (Te,Ce)O in the flow ammoxidation of propylene at 440°C (τ = 2.5 sec; C_3^- : NH_3 : air = 1 : 1 : 10).

similar data for the system TeO_2–MoO_3 have been reported elsewhere (*4*). Under these conditions CeO_2 converts some 55% of propylene with selectivities to ACN and acetonitrile of about 20% each. TeO_2 shows a slightly higher propylene conversion but a considerably higher ACN selectivity (about 70%) and forms negligible amounts of acetonitrile. The (Te,Ce)O/SiO_2 catalysts, which originate from oxides with a high and low selectivity to ACN (TeO_2 and CeO_2, respectively) show an intermediate behaviour as compared to the two extremes. The catalytic activity appears to be insensitive to composition other than at 75–80 mole% TeO_2, where it shows a maximum. Selectivities to ACN increase steadily from CeO_2 to the molar ratio $TeO_2/CeO_2 \approx 1$ and then level off at values close to those of TeO_2. Selectivities to acetonitrile and carbon oxides show the opposite trend; no acrolein was detected.

Morphology

Marked structural differences were evidenced in the (Te,Ce)O catalyst samples prepared by impregnation of microspheroidal silica. Variation in morphological properties with composition is given in Figs. 2 and 3 in terms of surface area (*SA*), pore volume (V_p), and integral distribution of the pore volume of the $(Ce_1Te_3)O/SiO_2$ composition. Both *SA* and V_p are constant over a wide composition range reaching extreme values for high tellurium contents (>80 mole% TeO_2). The 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.

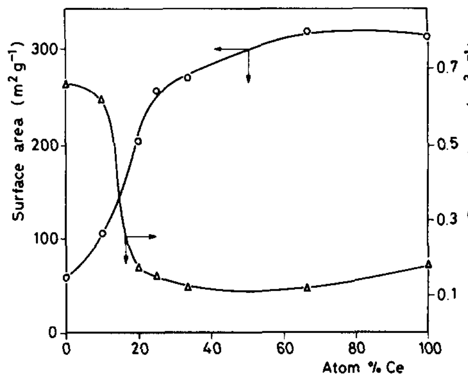

FIG. 2. Surface areas and pore volumes of SiO_2-supported CeO_2–TeO_2 catalysts calcined at 500°C for 8 h.

Phase Analysis

X-Ray diffraction of the SiO_2-supported (Te,Ce)O system reveals a fluorite-type solid solution with lattice parameter varying gradually with tellurium content from *a*

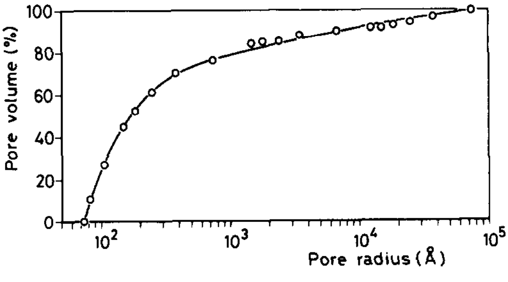

FIG. 3. Integral distribution of the pore volume of the $(Ce_1Te_3)O/SiO_2$ catalyst calcined at 500°C for 8 h.

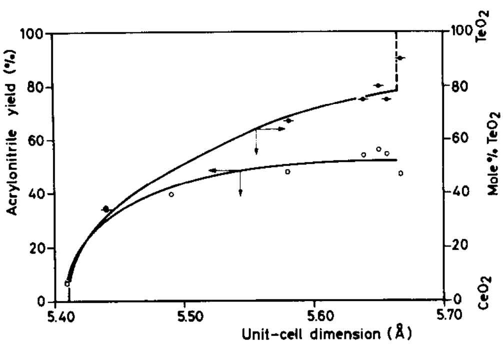

FIG. 4. Variation of unit-cell dimensions of SiO_2-supported fluorite-type $(Ce,Te)O_2$ solid solutions with composition (right scale); and acrylonitrile yield at 440°C under standard conditions as a function of the lattice parameter of $(Ce,Te)O_2$ (left scale).

= 5.411 Å in CeO_2 (ASTM 4-0593) up to a limiting value at about 80 mole% TeO_2 (Fig. 4) and the presence of a second phase, α-TeO_2 (ASTM 11-693), at higher compositions. The tellurium-saturated $(Ce,Te)O_2$ solid solution has a unit-cell constant of 5.666(3) Å, in accordance with previous findings (*12*).

DISCUSSION

X-Ray phase analysis of the impregnated $(Te,Ce)O/SiO_2$ catalysts calcined at 500°C for 8 h presents a much less complex pattern than that found for the previously described (Te,Ce)O system at the same temperature (*12*) where CeO_2, TeO_2, cerous tellurate, and tellurium-saturated and unsaturated $(Ce,Te)O_2$ solid solutions coexist. The observed phase distribution is reminiscent of the situation encountered in the (Te,Ce)O system at 450°C. This result is not quite unexpected as it has been found in other cases (e.g., in the thermal degradation of H_6TeO_6 as compared to H_6TeO_6/SiO_2) that the high degree of dispersion provided by silica influences (delays) chemical phenomena, the support having a stabilizing function. Nevertheless, there are important differences between the phase distributions in $(Te,Ce)O/SiO_2$ at 500°C and those in (Te,Ce)O at 450°C. Thus, instead of having CeO_2 and the tellurium-saturated solid solution in varying amounts in (Te,Ce)O at 450°C (cf. Fig. 1 of Ref. (*12*)), in the case of $(Te,Ce)O/SiO_2$ at 500°C we deal with a single nonstoichiometric cubic phase α-$(Ce,Te)O_2$ in a wide composition range, reaching saturation at about 80 mole% TeO_2 and exhibiting additionally free α-TeO_2 at higher compositions. This phase distribution greatly facilitates the interpretation of the morphological and catalytic activity data. In this respect, it appears reasonable to attribute the constant surface area and pore volume values of Fig. 2 to the nonstoichiometric α- and β-$(Ce,Te)O_2$ phases and the drastic changes to the influence of free paratellurite.

It may be argued that our data do not determine unequivocally the solubility limit of TeO_2 in CeO_2 as tellurium may partly be present in a finely dispersed state as α-TeO_2 or as amorphous or microcrystalline decomposition products of H_6TeO_6 with an unknown fraction really affecting the CeO_2 lattice. However, the detection of α-TeO_2 as a separate phase once the upper limit in the fluorite lattice parameter has been reached is quite significant. This result differs from the observations in the silica-free (Te,Ce)O system, where β-$(Ce,Te)O_2$ had already been formed at 450°C; at this temperature free α-TeO_2 is known to form only in appreciable quantities by degradation of H_6TeO_6 after considerably longer calcination than 8 h.

It should be mentioned that we have also succeeded in obtaining unsupported α-$(Ce,Te)O_2$ according to the procedure of Gusel'nikov *et al.* (*13*), starting from precipitates containing Ce(III) and Te(VI) in various formal ratios. It was verified that formation of α-$(Ce,Te)O_2$ sets in already at about 400°C, as shown in Table 1. We notice that the lattice parameter of α-$(Ce,Te)O_2$ of 5.436(6) Å, obtained for the formal composition $(Ce_2Te_1)O$, closely corresponds to the value expected from Fig. 4. On the other hand, precipitate $(Ce_1Te_1)O$ showed a = 5.551(6) Å (after 2 h at 500°C), as would rather be expected for a 62 mole% TeO_2

TABLE 1

Phase Analysis of Cerous Tellurate Precipitates

Precipitate atomic ratio Ce/Te[a]	Activation conditions		Phase analysis[b]	
	t (h)	T (°C)	α-(Ce,Te)O_2	$Ce_2(TeO_4)_3$
2:1	8	400	5.424(9)	–
2:1	2	500	5.436(6)	–
1:1[c]	2	500	5.551(6)	+[d]
1:1[c]	8	500	—	+
2:3	2	500	5.522(6)	–

[a] Refers to atomic ratio in solution.

[b] +, present; –, absent; for the fluorite phase the unit-cell dimension (Å) is given.

[c] Chemical analysis of the final product indicated Ce : Te = 2 : 3.

[d] Minor amounts.

concentration. Additional calcination (8 h at 500°C) of this sample (analyzed as $Ce_2Te_3O_{10}$ or $(Ce_{0.4}Te_{0.6})O_2$) led to the previously reported oxidation product for which chemical analysis suggested $Ce_2^{III}Te_3^{VI}O_{12}$ or $Ce_2(TeO_4)_3$ (*12*). This product differs from the white precipitate of identical stoichiometry described by Montignie (*14*). Activation of the precipitates at 550°C led to the formation of $CeTe_2O_6$. These results are all in good qualitative agreement with Fig. 1 of Ref. (*12*).

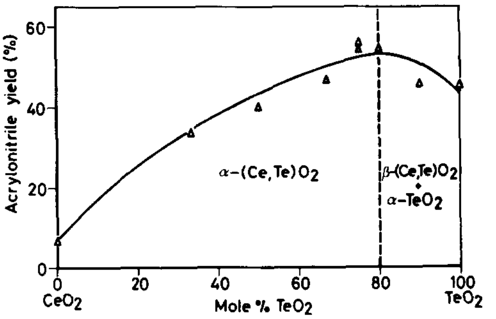

FIG. 5. Acrylonitrile yield at 440°C under standard flow conditions as a function of the tellurium content of (Te,Ce)O/SiO_2 catalysts.

The results of the catalytic activity measurements indicate a gradual increase in ACN yield with the unit-cell constants of the (Ce,Te)O_2 solid solution (Fig. 4) and an almost linear variation with the tellurium content (Fig. 5). At the limiting stage the product obtained, β-(Ce,Te)O_2, is more active than similarly SiO_2-supported paratellurite. Actually, with its 76.7% of propylene conversion and 74% of ACN selectivity the compound is amongst the most active (Te,M)O systems (*5*). The promotional effect of tellurium on cerium oxide is particularly significant as there are no changes in crystal structure involved. In view of the strong overoxidation tendency of CeO_2, as already observed by Minachev *et al.* (*15*), the function of tellurium is likely to be that of reducing this feature to more moderate proportions, leading to more useful technical applications.

It should be mentioned here that the not very pronounced maximum of conversion at about 75 mole% TeO_2 (Fig. 1) had originally been taken (*10*) as indicating the action of a previously described compound, $CeTe_3O_8$ (*16, 17*). This is now definitely ruled out and also does not fit related work (*12*).

Performance of the (Te,Ce)O system in the ammoxidation of propylene thus turns out to be quite different from that observed in the (Te,Mo)O system which presents typical features of "adlineation" promotion due to a high fraction of Te_2MoO_7 at the catalyst surface (*4*). The third component oxide system of the (Ce,Mo,Te)O catalyst, namely, the binary system (Ce,Mo)O, performs rather more poorly in oxidation catalysis (*6*).

CONCLUSIONS

Calcination at 500°C of silica-supported (Te,Ce)O induces some drastic variations in morphology (porosity, surface area) with tellurium content. X-Ray phase analysis supports a model for binary oxide samples consisting of a single nonstoichiometric phase α-(Ce,Te)O_2 up to 80 mole% TeO_2 and β-(Ce,Te)O_2 together with α-TeO_2 at higher tellurium concentrations. The ammoxidation activity of propylene varies almost linearly with the tellurium content of α-(Ce,Te)O_2.

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