

Influence of Bulk and Surface Structure of Tungsten Trioxide in the Oxidation of Propene

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Four samples of pure tungsten trioxide microcrystals were investigated for partial catalytic oxidation of propene by air at 375°C in a flow reactor at low conversion. Two of these catalysts were hexagonal WO_3 with well-developed (100) and (001) crystal faces, respectively. The other two were monoclinic WO_3 and differed only by their particle habits and specific surface areas and had well-developed (100) crystal faces. It was found that all the samples are selective for acrolein formation. The activity and selectivity are significantly different for the two hexagonal catalysts which differ by their exposed faces; as expected they are the same for the monoclinic samples. Selectivity appears to be equal for samples of different bulk structures but similar surface arrangements, i.e., WO_3 hex. (100) and WO_3 mono. (100); this correlation is not observed for activity.

INTRODUCTION

Crystal plane specificity has been investigated thoroughly in catalysis by metals (1), but experiments dealing with this topic for oxide catalysts were reported only recently (2), and concerned catalytic oxidation. The specific activity of oxides is generally low compared with that of metals and work with single crystals of very small surface area is therefore difficult. Valuable information may be obtained using powdered oxides of moderate surface area provided that for a given catalyst, samples made up of particles with well-developed crystal faces can be prepared.

During the study of the reactivity of tungsten trioxide hydrates we obtained several specimens of WO_3 with particles of different well-characterized habits. In this work we investigate the oxidation of propene on these WO_3 samples in order to determine the influence of surface structure on the activity and the selectivity for acrolein of tungsten trioxide for this reaction.

The selectivity of WO_3 for the oxidation

of propene into acrolein appears controversial. Most authors find acrolein in the reaction products (10-12). In a recent investigation involving nonstoichiometric tungsten oxides, the aim of which was to correlate the catalytic properties with the presence of crystallographic shear planes, De Rossi *et al.* (13) conclude that stoichiometric WO_3 is not selective for acrolein formation. For our part, although CO_2 was the major product, all our WO_3 samples yielded some acrolein.

EXPERIMENTAL

1. Preparation and Characterization of WO_3 Catalysts

At room temperature WO_3 has a monoclinic structure (3) but recently we prepared a hexagonal form (4) by dehydration of the hydrate $WO_3 \cdot \frac{1}{3}H_2O$ in air. This hydrate was prepared by hydrothermal treatment at 120°C of either $WO_3 \cdot 2H_2O$ or an acid tungstic gel (4). These two preparations lead to two types of habit for the particles of hexagonal WO_3 : thin octagonal

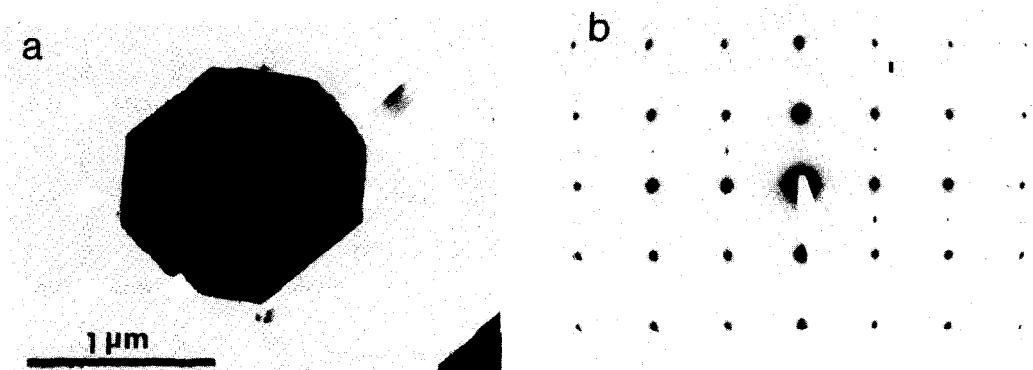


FIG. 1a. Thin octagonal platelets of hexagonal WO_3 : particles lying on the (100) plane as shown from the electron microdiffraction pattern.

FIG. 1b. Electron microdiffraction taken from a particle shown in Fig. 1a: the $(210)^*$ reciprocal section.

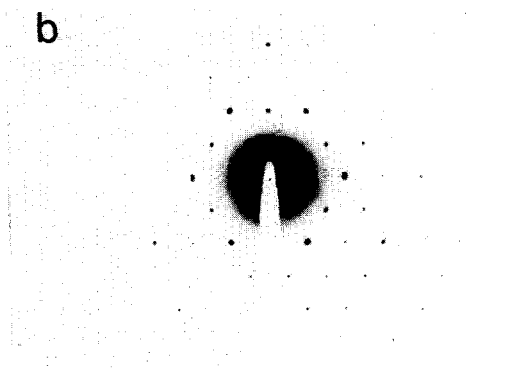
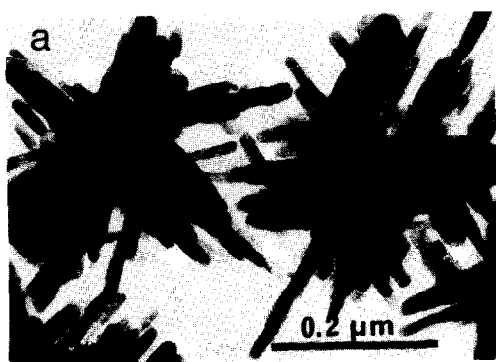


FIG. 2a. Thin flat needle crystals of hexagonal WO_3 lying on the (001) plane.

FIG. 2b. Electron microdiffraction from a particle of Fig. 2a: the $(001)^*$ reciprocal section.

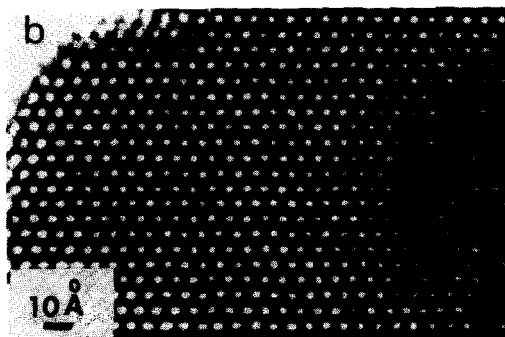
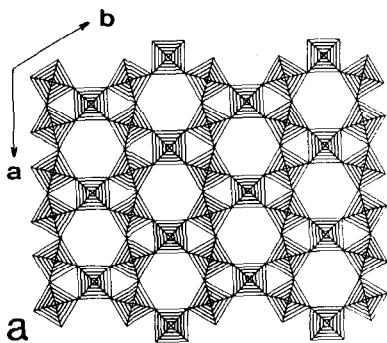


FIG. 3a. Schematic crystal structure of hexagonal WO_3 projected along the [001] axis.

FIG. 3b. HRTEM image of a thin portion of a crystal of hexagonal WO_3 lying on the (001) plane (see Fig. 2a). The correspondence of the lattice image with the idealized model of Fig. 3a is apparent.

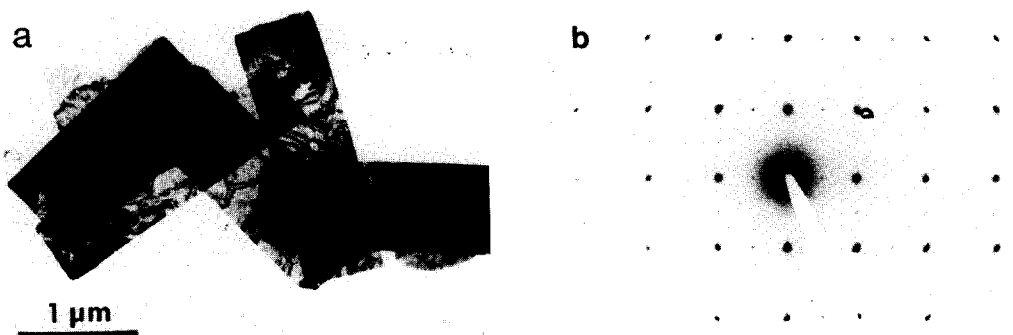


FIG. 4a. Thin rectangular platelets of monoclinic WO_3 lying on the (100) plane.

FIG. 4b. Electron microdiffraction from a particle of Fig. 4a or 5 showing that the particles are on the (100) plane.

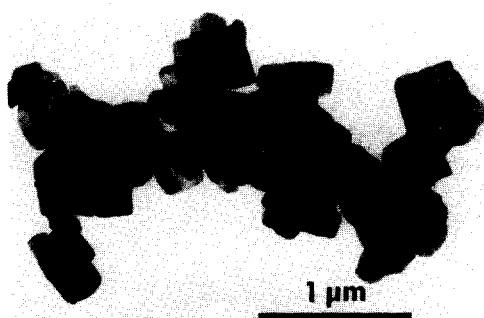


FIG. 5. Square thin platelets of monoclinic WO_3 lying on the (100) plane.

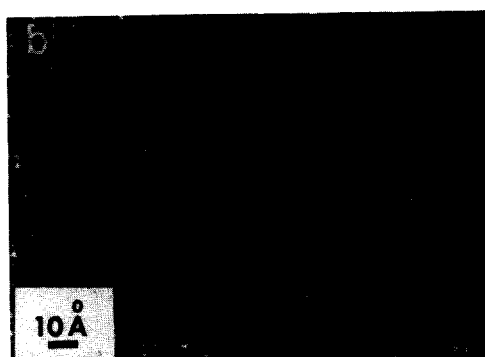
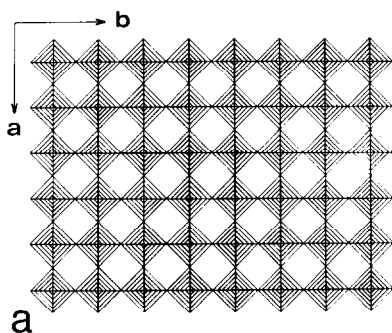


FIG. 6a. The schematic structure of monoclinic WO_3 projected along the c axis.

FIG. 6b. HRTEM image of a thin portion of a monoclinic WO_3 crystal lying on the (100) plane (Fig. 4a). The contrast distribution is in good accordance with the ideal structure projected on the (100) plane (Fig. 6a).

platelets lying on the (100) plane (Figs. 1a and b) and flat needle-like crystals lying on the (001) plane (Figs. 2a and b).

The structural study (4) of hexagonal WO_3 shows that it consists of a framework of slightly distorted (WO_6) octahedra exchanging corners and forming six-membered rings in the (001) plane (Fig. 3), defining hexagonal tunnels along [001].

For comparison we also investigated two types of monoclinic WO_3 particles. One with large thin rectangular platelets (Fig. 4a) lying on the (100) plane (Fig. 4b) was obtained by dehydration in air at about 300°C of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ prepared according to the method of Furusawa and Hachisu (5); the other was constituted of smaller square thin platelets (Fig. 5) with the same (100) orientation prepared with the dihydrate obtained by the method of Freedman (6). These two monoclinic samples differ only by their specific surface area.

The structure of the monoclinic form presents a regular array of slightly distorted, linked WO_6 octahedra (Fig. 6a). It may be noted that the surface structure of the (100) face of hexagonal WO_3 [WO_3 hex. (100)], and that of the (100) face of monoclinic WO_3 [WO_3 mono. (100)], are very similar; they differ only by the distortions of the WO_6 octahedra.

Each of these samples was characterized before and after catalytic reaction by X-ray diffraction (phase determination), electron microscopy (particle habit), electron microdiffraction, and HRTEM (high-resolution transmission electron microscopy) (particle orientation, crystal structure imaging, defects).

2. Catalytic Experiments

The experiments were carried out with a classical flow reactor operated at low conversion. The analytical system used has been described previously (7). The products detected were acrolein, carbon oxides, ethanal, and propanal. Carbon, oxygen, and hydrogen balances were equilibrated to within 10%.

The selectivity for propene oxidation was determined at zero conversion. This primary selectivity is not affected by the influence of secondary reactions of combustion of the products and is a better representation of the properties of the catalyst than results obtained at high conversion (8).

The primary selectivity was obtained by plotting individual yields of the products as a function of the conversion (Fig. 7). A linear relation is observed up to 4–5% conversion. This plotting using up to eight points ensures a good reliability for the selectivities determined at zero conversion (Fig. 7). Each point corresponds to the average of at least three runs with a good reproducibility. Two different masses of a given catalyst were used leading to quasi-identical results, as can be seen from Fig. 7. The reliability of the results is confirmed by the fact that both monoclinic samples, which differ only by their specific surface area, have similar selectivities and specific activities (Table 1).

RESULTS AND DISCUSSION

Propene oxidation was carried out at the lowest possible temperature to avoid structural modification of hexagonal WO_3 . Hexagonal WO_3 transforms irreversibly into the monoclinic form at about 400°C ; however, the transformation proceeds slowly, and at

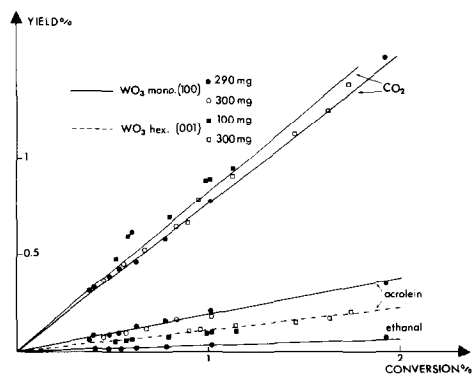


FIG. 7. Yield of the oxidation products as a function of propene conversion for different weights of two WO_3 catalysts: WO_3 mono. (100) and WO_3 hex. (001).

TABLE 1

The Influence of Bulk and Surface Structures on Catalytic Properties of Tungsten Trioxide for the Oxidation of Propene

	WO ₃ mono. (100) rectangular platelets (Fig. 4a)	WO ₃ mono. (100) square platelets (Fig. 5)	WO ₃ hex. (100) octagonal platelets (Fig. 1a)	WO ₃ hex. (001) needle-like crystals (Fig. 2a)
Structure	Monoclinic	Monoclinic	Hexagonal	Hexagonal
Developed crystal faces	(100)	(100)	(100)	(001)
Surface structure	Fig. 6a	Fig. 6a	Fig. 6a	Fig. 3a
Specific surface area (m ² g ⁻¹)	5.6	23.1	3.5	22.6
Selectivities (%)				
To acrolein	18	19	22	10
To CO ₂	77	76	71	86
Specific activities ^a (× 10 ⁸ mol. s ⁻¹ m ⁻²)				
C ₃ H ₆ oxidation	2	1.77	4.8	2
Acrolein formation	0.36	0.35	1	0.2

Note. Experimental conditions: $T = 375^{\circ}\text{C}$; reactant mixture C₃H₆/O₂/N₂ = 1/1/5.6.

^a Determined at a flow rate of 2.7 liters h⁻¹.

430°C the phase transition takes 100 h to complete (9). At 375°C, the temperature of the catalytic experiments, only very small amounts of monoclinic WO₃ were detected in hexagonal samples by X-ray diffraction and HRTEM. No change of the catalytic properties was observed during 24 h (which corresponds to eight different points repeated three times for each particular flow rate).

The experimental results are given in Table 1. The selectivity obtained here for propene oxidation into acrolein is in accordance with the results of the literature, since most authors find a more or less large amount of acrolein in the reaction products (10–12). As a borderline case, De Rossi *et al.* (13) do not find any acrolein at all; they claim that stoichiometric WO₃ is not selective for acrolein and that selectivity appears only on nonstoichiometric compounds such as WO_{2.95} and WO_{2.90} which are characterized by the presence of crystallographic shear planes. As a rule, selectivity decreases when conversion and temperature increase, because acrolein may undergo

further oxidation to carbon oxides, as is evident, for example, from the results of Germain and Perez (11). A simple explanation of the discrepancies observed in the literature may therefore be found in the experimental conditions, mainly in the high conversions used; so in this case the need to determine the primary selectivity has to be emphasized.

The examination of our catalysts, before and after catalytic reaction, by HRTEM (Figs. 3b and 6b) and electron microdiffraction shows the complete absence of crystallographic shear planes. Therefore the observed selectivity is, under our experimental conditions, due to stoichiometric WO₃.

As is shown in Table 1, the selectivity of WO₃ reaches at best 22%. A clear difference appears between the two catalysts presenting the hexagonal structure and different exposed planes: WO₃ hex. (100), which exhibits the (100) plane, yields a selectivity of 22%, while WO₃ hex. (001), with (001) orientation, yields a lower selectivity of 10%.

Significant differences of specific activity also appear.

On both monoclinic samples, which differ only by their specific surface area, the selectivities and specific activities are similar, as would be expected.

These experiments demonstrate clearly the influence of the surface structure on the catalytic properties of WO_3 for the oxidation of propene. The two hexagonal catalysts, which differ only by the developed crystal faces, give different activities and selectivities. The two monoclinic samples differ from the hexagonal ones either in selectivity or activity. It seems, at least in the case studied here of the oxidation of propene on WO_3 , that the selectivity is the same for samples of different structures provided that a similar surface arrangement (surface structure) is presented by the catalyst. This correlation is not observed for activity; with similar surface structure the activity is sensitive to the bulk structure.

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