Partial Oxidation of Propene over U.V.-irradiated Vanadium Oxide supported on Silica

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Summary Photocatalytically inactive V_2O_5 became highly active for the oxidation of propene when supported on SiO_2, and aldehydes were selectively formed even when the levels of conversion of propene were high.

PHOTOCATALYTIC oxidation over n-type semiconductors is of current interest, but there are only a few published studies on the oxidation of hydrocarbons.[1] Particularly, little work has been done on the oxidation of alkenes, although the intermediate formation of alkenes has been proposed in the oxidation of alkanes or alcohols.[2] Recently, Pichat *et al.*[3] have reported that propene was photocatalytically oxidised over various oxides, among which TiO_2 was the most active and V_2O_5 was photoinactive. We report herein that V_2O_5 supported on SiO_2 was effective for the partial oxidation of propene to aldehydes under u.v. irradiation, even at high levels of conversion of propene.

TABLE. Oxidation of propene over V_2O_5 on SiO_2 and TiO_2 under u.v. irradiation.[a]

							Products (mol %)[e]			
Expt.	Catalyst[b]	U.v. irradiation	T[c] (K)	Propene (μmol)	Oxygen (μmol)	Conversion[d] (%)	CH_3CHO	CH_3CH_2CHO	CH_2=CHCHO	Others
1	A	u.v.	320	54·4	66·7	0·81	trace	trace	trace	*ca.* 100
2	B	dark	320	41·0	45·8	2·9	0	0	0	2·9
3	B	u.v.	320	37·5	38·4	41·5	41·4	8·2	31·8	18·6
4	B	u.v.[f]	320	40·4	42·6	32·3	38·2	6·5	19·0	36·3
5	B	dark	373	37·0	46·5	4·4	2·2	2·2	4·5	90·9
6	B	u.v.	373	40·2	42·3	28·1	41·6	7·1	35·6	15·6
7	B	dark	473	44·6	54·7	19·0	29·5	7·3	26·8	36·3
8	C	u.v.	320	50·0	54·0	21·2	1·2	trace	2·5	96·2
9	D	u.v.	320	38·5	41·4	3·5	trace	trace	0·3	99·7

[a] Catalyst 500 mg; irradiated area 12 cm^2; propene and oxygen were mixed before introduction into the reactor; reaction time 0·5 h. [b] A, V_2O_5; B, V_2O_5 on SiO_2 (5 wt % V_2O_5); C, TiO_2; D, V_2O_5 on TiO_2 (5 wt % V_2O_5). [c] Temperature was that of the atmosphere just above the catalyst. [d] Based on propene introduced into the reactor. [e] Products were frozen out in a liquid-nitrogen trap in the dark in the three steps by varying the temperature of the catalyst: (i), at the reaction temperature without evacuation, followed by a short evacuation; (ii), the catalyst was heated up to 473 K; and (iii), to 573 K. The bulk of the aldehydes was collected in the second step, *e.g.* in Expt. 3 the aldehydes collected in each step amounted to 13, 78, and 10%, respectively, of the total amount of aldehydes collected. Trace constituents which were detected were acetone, propene oxide, formaldehyde, methane, and n-hexane. The loss of yield (other products) was mainly due to CO_2 and polymeric compounds which were not desorbed at 573 K. The latter were completely oxidised at 673 K and estimated from the amounts of CO_2 produced. Total carbon balance based on propene was 101·5% (Expt. 3). [f] The catalyst was pre-reduced by photoreduction under a CO atmosphere (ref. 5).

The catalyst was prepared as described previously.[4] The content of V_2O_5 was 5 wt%. Reactions were performed in a conventional gas-circulating system with a quartz reactor,[5] and a xenon lamp (USHIO UXL-500) was used for the irradiation. The catalyst was irradiated for 0·5 h in an atmosphere of propene and oxygen, and the products were collected in a trap at 77 K and analysed by g.l.c. Results are given in the Table. No product was detected in the photoreaction without the catalyst. Propene was little oxidised using V_2O_5 on SiO_2 in the dark at 320 or 373 K and only slowly at 473 K. The u.v. irradiation undoubtedly promoted oxidation and the partial oxidation products, *i.e.* ethanal, acrylaldehyde, and propanal, were the main products, and not carbon dioxide, even at high levels of conversion of propene.

Pichat *et al.*[3] reported that the ratio of CO_2:partial oxidation products using TiO_2 was 3:2, even at 0·055% conversion at 320 K. Conversion under the conditions described herein, using TiO_2, was 21·2% (Expt. 8), but the partial oxidation products constituted only a small percentage of the conversion products. It is also clear that photoinactive V_2O_5 becomes active when supported on SiO_2, but not on TiO_2 (Expt. 9). The product distribution, ethanal > acrylaldehyde $\gg$ propanal, was different from that in the oxidation by O_2^- (adsorbed) over V_2O_5 on SiO_2, propanal > ethanal $\gg$ acrylaldehyde.[4] Pre-reduction of the catalyst by CO (Expt. 4) resulted in a decrease in the conversion of propene and formation of acrylaldehyde.

These results suggest that an oxygen species other than O_2^- participates in the photo-oxidation of propene. Since the pre-reduction not only increases the O_2^- species,[4] but also decreases the lattice oxygen species, lattice oxygen activated by photons seems to be the probable oxygen species. The direct participation of the lattice oxygen in the photoirradiation has been shown in the photoreaction of CO.[5] Kazansky *et al.* have proposed photoactivation of the lattice oxygen by charge transfer from the lattice oxygen to a metal ion[6] and supposed that the activated oxygen is an active centre for the oxidation of methane and ethane.[7] The result that the bulk of aldehydes was collected when the catalyst was heated to 473 K to collect the products may indicate that a major part of the changed propene is converted into surface complexes over the photoirradiated catalyst and is then thermally decomposed to aldehydes during the procedure used to collect the products, but it seems very difficult to differentiate quantitatively the surface complexes from strongly held aldehydes which might be formed without the aid of thermal treatment.

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