# Activity and Selectivity in Toluene Oxidation on Well Characterized Vanadium Oxide Catalysts

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Activity and selectivity in the oxidation of toluene on unsupported and supported  $V_2O_5$  catalysts  $(V_2O_5/TiO_2 \text{ and } V_2O_5/Al_2O_3)$  have been investigated in terms of the catalyst structure under the following conditions: total pressure, 1 atm (1 atm  $\approx$  101.3 kPa); partial pressure of toluene, 0.041 atm; partial pressure of O<sub>2</sub>, 0-0.861 atm; temperature, 588-644 K. The results under various contact times indicated that partial oxidation to benzaldehyde, benzoic acid and maleic anhydride proceeds concurrently with the total oxidation to carbon oxides on the vanadium oxide catalyst. It was also found that the surface V=O species plays the active oxygen species and that the activity is mainly determined by the number of surface V=O species for both unsupported and supported catalysts. Although the selectivity to partial oxidation products  $(S_p)$  was independent of the oxidation state of the vanadium oxide, it was greatly affected by the roughness of the catalyst surface and rough V<sub>2</sub>O<sub>5</sub> was favourable for the selective oxidation. This provides a new type of structure-selectivity correlation for the vanadium oxide and has never been observed for the oxidation of benzene, but-1-ene, buta-1,3-diene or furan. In agreement with the correlation, the mode of change in the selectivity with the structure of supported catalysts was much different from that for previous reactions and was explained in terms of the change in surface roughness. A mechanism is also proposed to explain the new structure-activity/selectivity correlation for the toluene oxidation.

Supported metal oxides exhibit interesting catalytic behaviour depending on the kind of support, the content of active component and the preparation method.<sup>1</sup> However, the activity and selectivity on the supported metal-oxide catalyst have not been clarified in terms of the structure of the metal oxide on the support. This is due to the lack of a well established method to determine the structure of such catalysts and, more especially, the number of active sites.<sup>2</sup> For supported vanadium oxide catalysts, we have previously established the rectangular-pulse technique, which allows the determination of the number of surface V=O species and the number of  $V_2O_5$  layers on the support.<sup>3</sup> Furthermore, the structures of  $V_2O_5/TiO_2$  and  $V_2O_5/Al_2O_3$  catalysts have been determined by various physicochemical measurements together with the rectangular-pulse technique.<sup>4</sup> By investigating the oxidation of  $CO^{5a}$  and  $H_2^{5b}$  (simple diatomic molecules), n-butane<sup>5c</sup> (a saturated hydrocarbon), ethene and but-1-ene<sup>5e</sup> (alkenes), buta-1,3-diene<sup>5e</sup> (a diene), furan<sup>5f</sup> (an oxygen-containing molecule), and benzene<sup>5g</sup> (an aromatic molecule), the reduction of NO with  $NH_3^{5h}$ , and the isomerization of but-1-ene

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### Toluene Oxidation on Vanadium Oxide Catalysts

to but-2-ene<sup>5e</sup> on well characterized vanadium oxide catalysts, we have revealed some important factors for understanding the catalysis of vanadium oxides, such as (i) active oxygen species; the effects of (ii) the oxidation state, (iii) surface roughness and (iv) number of  $V_2O_5$  layers on the activity and selectivity; (v) the effect of the support on both the number of active sites and the turnover frequency, and (vi) the effect of the type of reaction on activation.<sup>5,6</sup> These studies also indicate that catalysis of vanadium oxide changes significantly, depending on the structure of the reactant molecule or the type of reaction, a behaviour similar to enzyme action. A small change in the structure of the reactant molecule sometimes leads to a large change in the catalytic behaviour. Thus, more information about the structure–activity/selectivity correlation is necessary to form general ideas about the catalysis of supported vanadium oxides.

The purpose of this study is to clarify the structure–activity/selectivity correlation for toluene oxidation on well characterized vanadium oxides and discuss the result in comparison with those for previous reactions. Toluene oxidation was chosen because toluene is the simplest alkylbenzene and the structure–activity/selectivity correlation for the oxidation of toluene would give important information about the catalysis by vanadium oxide of the oxidation of *o*-xylene (a dimethylbenzene). It would also be interesting to compare the structure–activity/selectivity correlation for toluene oxidation (a reaction of a benzene ring) with that for benzene oxidation (a reaction of the ring itself). Although a number of interesting and important results have been reported about the catalysis by vanadium oxide of its toluene oxidation,<sup>7</sup> structure–activity/selectivity correlation, for structure–activity/selectivity correlation.

# Experimental

### Catalysts

 $V_2O_5$ -U catalyst was prepared by thermal decomposition of  $NH_4VO_3$  at 773 K in flowing  $O_2$ .  $V_2O_5$ -F catalyst was prepared by fusing the  $V_2O_5$ -U catalyst at 1073 K for 18 h in air, followed by gradual cooling to room temperature.  $V_2O_5$ -RO catalyst was prepared from the  $V_2O_5$ -F catalyst by a reduction-oxidation treatment, *viz*. reduction in flowing  $H_2$  at 673 K for 1 h followed by reoxidation in flowing  $O_2$  (20%) at 673 K for 1 h, and this redox cycle was repeated 5 times. The number of surface V=O species (*L*) on the catalyst was determined by using the rectangular-pulse technique<sup>3</sup> and the results are shown in table 1 together with the results for the B.E.T. surface area ( $S_{BET}$ ). The number of  $V_2O_5$  layers (*N*) for the catalysts was calculated from *L* using the equation

$$N = 2/L[M(V_2O_5)] \tag{1}$$

where  $M(V_2O_5)$  is the molecular weight of  $V_2O_5$ . According to the results of X-ray diffraction, u.v.-visible spectra, i.r. spectra, X-ray photoelectron spectra and scanning electron micrographs of the catalysts,<sup>4a</sup> the electronic properties of the catalysts are the same, while the surfaces of  $V_2O_5$ -U and  $V_2O_5$ -RO are rougher than that of  $V_2O_5$ -F.

TiO<sub>2</sub> (anatase) was prepared by hydrolysis of Ti(SO<sub>4</sub>)<sub>2</sub> followed by calcination in air at 873 K, while Al<sub>2</sub>O<sub>3</sub> was commercially available (Sumitomo  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). The B.E.T. surface areas of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were 48 and 230 m<sup>2</sup> g<sup>-1</sup>, respectively. Vanadium oxides supported on the carrier were prepared by impregnation of the carrier with an oxalic acid solution of NH<sub>4</sub>VO<sub>3</sub> followed by calcination at 773 K in a stream of O<sub>2</sub> for 3 h. The *L*, *N* and S<sub>BET</sub> values of the supported catalysts are shown in table 2.  $M_L$  is the theoretical monolayer of V<sub>2</sub>O<sub>5</sub>,<sup>8</sup> which is calculated from the V<sub>2</sub>O<sub>5</sub> content (*x*) and S<sub>BET</sub> using the equation

$$M_{\rm L} = \frac{N x \sigma(V_2 O_5)}{x M(V_2 O_5) + (1 - x) M(\text{support}) S_{\rm BET}} \%$$
(2)

catalyst	$S_{\scriptscriptstyle m BET} \ /m^2  g^{-1}$	$L/\mu mol g^{-1}$	R / $\mu$ mol g <sup>-1</sup> s <sup>-1</sup>	$(R/S_{\rm BET})$ / $\mu$ mol m <sup>-2</sup> s <sup>-1</sup>	TOF /10 <sup>3</sup> s <sup>-1</sup>	S <sub>p</sub> (%)
V <sub>a</sub> O <sub>z</sub> -U	5.4	22	8.90	1.65	405	52
V <sub>3</sub> O <sub>5</sub> -F	0.8	4	1.33	1.66	333	26
V <sub>2</sub> O <sub>5</sub> -RO	0.8	4	1.43	1.78	356	37

Table 1. Physical and catalytic properties of unsupported V<sub>2</sub>O<sub>5</sub> catalysts<sup>a</sup>

<sup>a</sup>  $S_{\text{BET}}$  is the B.E.T. (Brunauer-Emmett-Teller) surface area, L is the number of surface V=O species, R is the reaction rate, TOF is the turnover frequency for the oxidation,  $S_p$  is the selectivity to partial oxidation products. Reaction conditions: T = 623 K;  $P_T = 0.041$  atm;  $P_O = 0.711$  atm.

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	catalyst (mol %)	$\frac{S_{\rm BET}}{/{\rm m}^2{\rm g}^{-1}}$	$L/\mu mol g^{-1}$	N	М <sub>ь</sub> (%)	$R/\mu mol g^{-1} s^{-1}$	TOF /10 <sup>3</sup> s <sup>-1</sup>	S <sub>p</sub> (%)
				V <sub>a</sub> O <sub>5</sub> /T	iO,			
	1	47.2	56	1-2	<b>3</b> 2	68.5	1223	0
	2	45.2	120	1–2	67	71.4	595	0
	5	26.3	184	2-3	280	79.6	433	12
	10	22.8	135	5–8	600	74.1	549	19
	25	10.3	60	30-40	2800	31.9	532	38
	50	7.4	31	50-60	6400	16.6	535	47
					0			
			•	$V_2O_5/AI$	<sub>2</sub> O <sub>3</sub>	6.05		•
	2	221.3	3	1-2	11	6.27	2090	0
	5	219.1	77	1–2	27	43.6	566	19
	10	167.6	355	1–3	67	184.1	518	27
	25	114.1	405	2–4	220	191.2	472	26
	35	101.1	365	3–7	330	143.1	392	25
	50	65.8	249	5-15	660	68.7	276	35
				$V_2O_5$ -1	U			
		5.4	22	504		8.90	405	52

Table 2. Physical and catalytic properties of  $V_2O_5/TiO_2$  and  $V_2O_5/Al_2O_3$  catalysts<sup>a</sup>

<sup>*a*</sup> N is the number of  $V_2O_5$  layers on the support.

where N is Avogadro's number,  $\sigma(V_2O_5)$  is the area occupied by a  $V_2O_5$  unit (20.6 Å<sup>2</sup>) and M(support) is the molecular weight of the support (TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>). Unless otherwise stated, the particle size of the catalyst was in the range 28–48 mesh.

### **Catalytic Activity Measurements**

Kinetic studies were carried out using the continuous flow reaction technique under the following conditions: total pressure = 1 atm, partial pressure of toluene = 0.041 atm, partial pressure of  $O_2(P_0) = 0-0.861$  atm, temperature = 588-644 K, and W/F = 71.4-2485 g s mol<sup>-1</sup>. Particular care was paid to eliminating the heat of reaction and therefore controlling the reaction temperature (±1 K). The glass reactor was heated to reaction temperature using a fluidized bed, and the catalyst was diluted with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The outlet gas was cooled using ice-cooled traps to separate liquid products from gas products and analysis was by gas chromatography. The liquid components (toluene, benzaldehyde, benzoic acid and maleic anhydride) were analysed using a 6 m × 3 mm i.d. column of 5% diethylene glycol succinate and 1% H<sub>3</sub>PO<sub>4</sub> on 60-80 mesh Chromosorb WAW at



**Fig. 1.** Production rates of products [(a), (b)] and selectivity (c) for the oxidation of toluene on  $V_2O_5$ -U. (a)  $\blacklozenge$ , CO;  $\diamondsuit$ , CO<sub>2</sub>; (b)  $\bigcirc$ , benzaldehyde;  $\blacklozenge$ , benzoic acid;  $\circlearrowright$ , maleic anhydride; (c)  $\bigcirc$ , selectivity. Reaction temperature = 610 K,  $P_T = 0.041$  atm;  $P_O = 0.711$  atm.

423 K with helium as a carrier gas (30 cm<sup>3</sup> min<sup>-1</sup>), while the gaseous components (N<sub>2</sub>, O<sub>2</sub>, CO and CO<sub>2</sub>) were analysed using a  $4 \text{ m} \times 3 \text{ mm}$  i.d. column of 30–60 mesh molecular sieve 13X and a  $4 \text{ m} \times 3 \text{ mm}$  i.d. column of 80–100 mesh Porapak Q at room temperature with helium as the carrier gas (30 cm<sup>3</sup> min<sup>-1</sup>).

### **Characterization of Catalysts**

A catalyst in the steady-state reaction was rapidly cooled to room temperature under inert gas flow  $(N_2)$  to measure the steady-state catalyst structure. I.r. spectra of the catalyst were recorded on a Jasco-EDR-31 i.r. diffuse reflectance spectrometer using KBr as diluent.<sup>9</sup>

### Results

# Influence of Contact Time on the Rates of Formation of Products

Products identified in the oxidation of toluene on vanadium oxides were benzaldehyde, benzoic acid, maleic anhydride, CO and CO<sub>2</sub>. Fig. 1 depicts the rate of formation of each product as a function of W/F, where W and F are the catalyst weight and flow rate, respectively. The production of benzaldehyde increased with increasing W/F to 800 g s mol<sup>-1</sup>, and decreased with further increase in W/F. The production of benzoic acid or maleic anhydride was not detected at low values of  $W/F(W/F = 300 \text{ g s mol}^{-1})$ , but was observed with  $W/F > 300 \text{ g sol}^{-1}$ . On the other hand, the rates of formation of CO and





**Fig. 2.** Effect of  $P_0$  on R, R(B), R(BA), R(MA),  $R(CO+CO_2)$  and  $S_p$  for  $V_2O_5$ -U. (a)  $\bigcirc$ ,  $R; (b) \bigcirc$ ,  $R(B); \bigcirc$ ,  $R(BA); \bigcirc$ ,  $R(MA); \diamondsuit$ ,  $R(CO+CO_2); (c) \bigcirc$ ,  $S_p$ . Reaction temperature = 615 K;  $P_T = 0.041$  atm.

 $CO_2$  gradually increased with increase in W/F. From these results, the oxidation of toluene is considered to proceed through the following paths:

namely, partial oxidation to benzaldehyde(B), benzoic acid(BA) and maleic anhydride(MA) [eqn (3)] proceeds concurrently with total oxidation to oxides of carbon [eqn (4)], while BA is produced consecutively from B and subsequently converted to MA. Taking into account the stoichiometries of eqn (3) and (4), the rates of formation of benzaldehyde [R(B)], benzoic acid[R(BA)], maleic anhydride[R(MA)] and oxides of carbon [ $R(CO + CO_2)$ ] are defined as the rates of toluene converted to each product. Furthermore, the total reaction rate(R) and the selectivity to partial oxidation products( $S_p$ ) are defined as follows:

$$R = R(B) + R(BA) + R(MA) + R(CO + CO_2)$$
(5)

$$S_{\rm p} = [R(B) + R(BA) + R(MA)]/R.$$
(6)

The relationship between the selectivity  $(S_p)$  and W/F is shown in fig. 1(c). It can be seen that  $S_p$  is independent of the contact time (W/F), indicating the validity of the reaction paths in eqn (3) and (4).

### Effect of Po on Reaction Rates and Catalyst Structures

Fig. 2 shows the effect of  $P_0$  on R, R(B), R(BA), R(MA),  $R(CO+CO_2)$  and  $S_p$  for  $V_2O_5$ -U. The rates increase monotonically with increasing  $P_0$  up to 0.47 atm and are



Fig. 3. Infrared spectra of the  $V_2O_5$ -U catalyst in the steady state of the reaction at various partial pressures of  $O_2$ . Temperature = 615 K;  $P_T = 0.041$  atm. The numbers beside the curves give the partial pressures of  $O_2$ .

almost constant for  $P_0 > 0.47$  atm. In spite of the change in the reaction rates with  $P_0$ ,  $S_p$  is independent of  $P_0$ , as shown in fig. 2(c).

Fig. 3 shows the i.r. spectra of  $V_2O_5$ -U in the steady-state reaction at various  $P_0$ . The catalyst under  $P_0$  of 0.70 and 0.86 atm gives absorption bands at 1020 and 825 cm<sup>-1</sup>, assigned to the stretching vibration of V=O species and the coupled vibration between V=O and V-O-V, respectively.<sup>10,11</sup> These spectra are the same as that of fresh  $V_2O_5$ -U. As for the catalyst under  $P_0$  of 0.475 and 0.25 atm, the absorption intensity at 1020 cm<sup>-1</sup> decreases. Moreover, new absorption bands at 990 and 910 cm<sup>-1</sup>, assigned to lattice vibration of  $V_2O_4$ ,<sup>12</sup> are observed for the catalysts in the steady-state reaction under  $P_0$  of 0.1 and 0.25 atm. In order to examine the quantitative change in the amount of V=O species at various  $P_0$ , absorbances at 1020 cm<sup>-1</sup> were calculated from the spectra in fig. 3 using the Kubelka-Munk equation, and the result is shown in fig. 4. The amount of V=O species in the catalyst increases monotonically with increasing  $P_0$  up to 0.70 atm, while it barely changes with a further increase in  $P_0$ .

#### Activity and Selectivity under Conditions of Excess Oxygen

Table 1 shows results of the toluene oxidation for unsupported  $V_2O_5$  catalysts under excess oxygen conditions where the reaction rate was zeroth order with respect to  $P_0$  and the catalyst was confirmed to be in the highest oxidation state, *i.e.* V<sup>5+</sup>. In accordance with the decrease in  $S_{BET}$ , R for  $V_2O_5$ -F or  $V_2O_5$ -RO is much smaller than that for  $V_2O_5$ -U. However, the specific rate as defined by  $R/S_{BET}$  is almost constant for these catalysts. In contrast to the behaviour of the reaction rate, the selectivity to partial oxidation product  $(S_p)$  changes greatly with the type of unsupported  $V_2O_5$ -RO is considerably higher than that for  $V_2O_5$ -F.



Fig. 4. Amount of V=O in the  $V_2O_5$ -U catalyst in the steady state of the reaction at various partial pressures of  $O_2$ .

Table 3. Effect of surface roughness on activity and selectivity in the various reactions on  $V_2O_5$  catalysts

reactant		activity	selectivity		
	toluene	insensitive	sensitive		
	benzene	insensitive	insensitive		
	but-1-ene	insensitive	insensitive		
	buta-1,3-diene	sensitive	insensitive		
	furan	sensitive	insensitive		

Table 2 shows results of R and  $S_p$  for  $V_2O_5/TiO_2$  and  $V_2O_5/Al_2O_3$  catalysts with various  $V_2O_5$  contents. TiO<sub>2</sub> or  $Al_2O_3$  alone had a negligible activity for the toluene oxidation. The reaction rate (R) for  $V_2O_5/TiO_2$  increases markedly with an increase in  $V_2O_5$  content from 0 to 5 mol%, passes a maximum at 5 mol%  $V_2O_5$ , and then decreases to the value of  $V_2O_5$ -U with further increase in  $V_2O_5$  content. In the case of  $V_2O_5/Al_2O_3$ , the 2 mol%  $V_2O_5$  content from 5 to 25 mol%. As for the selectivity, the total oxidation to oxides of carbon takes place preferentially when the  $V_2O_5$  content in  $V_2O_5/TiO_2$  is low (1 or 2 mol%). However,  $S_p$  increases gradually with the increase in  $V_2O_5$  content.  $S_p$  for  $V_2O_5/Al_2O_3$  with low  $V_2O_5$  content (2 or 5 mol%) is very low, while it increases with increasing  $V_2O_5$  content.

Although tables 1 and 2 show results for the reaction at 623 K, similar relationships were found to hold at any temperature between 588 and 644 K : the apparent activation energy for R was  $121-126 \text{ kJ mol}^{-1}$  for unsupported  $V_2O_5$  catalysts,  $105-117 \text{ kJ mol}^{-1}$  for  $V_2O_5/\text{Ti}O_2$ , and  $126-130 \text{ kJ mol}^{-1}$  for  $V_2O_5/\text{Al}_2O_3$ , respectively.

# Discussion

### Active Oxygen Species for Toluene Oxidation

As shown in fig. 2(*a*), the rate of toluene oxidation for  $V_2O_5$ -U increases monotonically with increasing  $P_0$  and attains a constant value above 0.47 atm of  $P_0$ . As shown in fig.

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4, the amount of V<sup>5+</sup>=O species in the catalysts in the steady-state reaction changes similarly with respect to the change in  $P_0$ . This suggests that the reaction proceeds by the reduction-oxidation mechanism (or Mars-van Krevelen mechanism)<sup>13</sup> and that the active oxygen species for the toluene oxidation is a surface V=O species. After stopping the O<sub>2</sub> gas supply, the reaction rate decreased gradually with time and attained a negligible value at 70 min after the reaction began. Adsorbed oxygen species  $(O_2^-, O^-)$  or  $O_{a^{-}}$ ) can be shown not to be responsible for the reaction under the present reaction conditions for the following reasons: no adsorbed oxygen species was detected on the catalyst by either e.s.r. or t.p.d. measurements; moreover, even if the surface of  $V_2O_3$ -U were initially covered completely with adsorbed oxygen species, these species would be consumed by the reaction with toluene molecules within a few seconds of stopping the oxygen supply and the rate would decrease abruptly, contradictory to the experimental result. Since the number of bulk V=O species in the catalyst is much larger than that of surface V=O species, the bulk V=O species can diffuse easily from the bulk to the surface of catalyst. When the oxygen supply is stopped, the surface V=O species are consumed by the reaction with toluene to form a reduced site ( $V^{4+}$  ion) and reaction products. The reduced site is then reoxidized by the bulk V=O species to form more surface V=O species; therefore the rate of toluene oxidation decreases gradually until all the bulk V=O species are consumed by the reaction.

### Structural Factors which Determine the Activity

In general, the activity is determined by two factors: (i) the number of active sites and (ii) the specific activity of the active site, *i.e.* the turnover frequency (TOF). The separation of these two factors is indispensable for a detailed understanding of the effect of catalyst structure on activity; however, this has not been done for the supported metal-oxide catalyst because of the lack of a well established method for determining the number of active sites. Since the number of surface V=O species (L) has been determined for the vanadium oxide catalysts and the species has been found to be an active oxygen species for the toluene oxidation, the effect of catalyst structure on activity can be discussed in terms of TOF defined by

$$TOF = R/L.$$
 (7)

Since the effect of support on the number of surface V=O species has been described elsewhere,<sup>4</sup> we will not discuss it in this paper. TOF values at 623 K were calculated from R and L for various catalysts and these are also shown in tables 1 and 2.

The surface of  $V_2O_5$ -F has been found to be significantly different from that of  $V_2O_5$ -U and  $V_2O_5$ -RO.<sup>5a</sup> The surface of  $V_2O_5$ -F is much smoother than that of  $V_2O_5$ -U or  $V_2O_5$ -RO. This is reasonable since fusion of a solid would generally lead to a smooth surface with a decreased number of surface defects (*e.g.* steps, kinks or vacancies), while severe redox treatment of a solid with few surface defects would tend to increase their number. No impurity peaks were observed in the X.p. spectra of  $V_2O_5$ -U,  $V_2O_5$ -F or  $V_2O_5$ -RO. In spite of the significant change in the surface structure among  $V_2O_5$ -U,  $V_2O_5$ -F and  $V_2O_5$ -RO, TOF does not differ significantly from one to another, suggesting that the roughness of the  $V_2O_5$  surface does not affect the activity for the toluene oxidation.

Except for the catalysts with low  $V_2O_5$  contents, *i.e.*  $V_2O_5/TiO_2$  (1 mol %  $V_2O_5$ ) and  $V_2O_5/Al_2O_3$  (2 mol %  $V_2O_5$ ), TOF for  $V_2O_5/TiO_2$  and  $V_2O_5/Al_2O_3$  is approximately constant and independent of the  $V_2O_5$  content or the kind of support (table 2). This indicates that the activity of supported vanadium oxides is mainly determined by the number of V=O species and that the promoting effect of  $Al_2O_3$  or TiO<sub>2</sub> is to increase the number of surface V=O species, but the specific activity of the surface V=O species is not increased.

According to our previous investigations, the activity for the oxidation of  $H_2^{5b}$  and the reduction of NO with  $NH_3$  in the presence of  $O_2^{5h}$  is determined only by the number of surface V=O species and is independent of the  $V_2O_5$  content or the kind of support. It has been suggested that the rate-determining step under the excess oxygen reaction is

$$\begin{array}{ccccccccc} O & O & OH & OH \\ \parallel & \parallel & & | & | \\ H_2 + -V - O - V - & \longrightarrow & -V - O - V - \end{array} \tag{8}$$

for the H<sub>2</sub> oxidation<sup>5b</sup> and

$$\begin{array}{c} O & OH \\ \parallel & \mid \\ NO + NH_3 + -V - \longrightarrow N_2 + H_2O + -V - \end{array}$$

$$(9)$$

for the reduction of NO with NH<sub>3</sub> in the presence of O<sub>2</sub>.<sup>14</sup> Since the role of V=O species in these reactions [eqn (8) and (9)] is to combine with hydrogen atoms released from the reactant molecule but not to donate the oxygen atom of V=O to the reactant molecule, the almost constant TOF for toluene oxidation suggests that the rate-determining step under excess oxygen conditions is the abstraction of a hydrogen atom from the methyl group of the toluene molecule. This is consistent with the TOF value for toluene oxidation, which is 7–20 times higher than TOF for benzene oxidation.<sup>5g</sup>

#### Structural Factors which Determine the Selectivity

As shown in fig. 3(c), the selectivity to partial oxidation products  $(S_p)$  is independent of the change in  $P_0$ . This means that  $S_p$  is not affected by the change in oxidation state of vanadium between  $V^{5+}$  and  $V^{4+}$ .

As shown in table 1, on the other hand, the selectivity to partial oxidation products  $(S_p)$  changes greatly with the type of unsupported  $V_2O_5$  catalyst. Namely, the value of  $S_p$  for  $V_2O_5$ -U is higher than that for  $V_2O_5$ -F, while that for  $V_2O_5$ -RO is larger than that for  $V_2O_5$ -F. This suggests that the rough  $V_2O_5$  surface with many surface defects is effective for selective oxidation, while the smooth  $V_2O_5$  surface without surface defects leads to the total oxidation to carbon oxides. Although the selectivity in the oxidation of but-1-ene, buta-1,3-diene, furan and benzene has been investigated on the same vanadium oxide catalysts, the effect of roughness of the catalyst surface on the selectivity has never been observed<sup>5, 6</sup> and provides a new type of structure-selectivity correlation for vanadium oxide catalysts.

According to our previous investigations of the oxidation of but-1-ene, buta-1,3diene, furan and benzene on supported vanadium oxide catalysts,<sup>5,6</sup> the selectivity to the partial oxidation product  $(S_p)$  was best represented as a function of the number of  $V_2O_5$  layers on the support (N); some examples of the correlations are shown in fig. 5. When N is 1 or 2, the selectivity is low, while it increases markedly with increase in N and attains a constant value above 5 layers. It should be noted that the correlation is common to both  $V_2O_5/TiO_2$  and  $V_2O_5/Al_2O_3$  in spite of the significant difference in the structure between  $\bar{V}_2 O_5 / Ti O_2$  and  $\bar{V}_2 O_5 / Al_2 O_3$ . Thus,  $S_p$  was also plotted against N for the toluene oxidation (fig. 6). As shown in fig. 6, the relationship between  $S_p$  and N for toluene oxidation is very different from that for the oxidation of benzene, but-1-ene and buta-1,3-diene shown in fig. 5. Note also that the relationship for  $V_2O_5/TiO_2$  is different from that for  $V_2O_5/Al_2O_3$ . These results indicate that the number of  $V_2O_5$  layers (N) is not an appropriate structural parameter to determine the selectivity in toluene oxidation. This is consistent with the abovementioned conclusion that toluene oxidation exhibits a new type of structure-selectivity correlation; namely, the rough V<sub>2</sub>O<sub>5</sub> surface with surface defects such as steps, kinks or vacancies is favourable for the selective oxidation to benzaldehyde, benzoic acid and maleic anhydride. Although the important





**Fig. 5.** Relationship between the selectivity and the number of  $V_2O_5$  layers on the support for the oxidations of benzene (a), but-1-ene (b) and buta-1,3-diene (c).  $\bigcirc$ ,  $V_2O_5/TiO_2$ ;  $\triangle$ ,  $V_2O_5/Al_2O_3$ ;  $\diamondsuit$ ,  $V_2O_5-U$ .



**Fig. 6.** Relationship between the selectivity and the number of  $V_2O_5$  layers on the support.  $\bigcirc, V_2O_5/\text{TiO}_2; \triangle, V_2O_5/\text{Al}_2O_3; \bigoplus, V_2O_5-\text{U}.$ 

effect of surface roughness on the selectivity is a new finding in toluene oxidation, a significant effect of surface roughness on TOF has already been found for the oxidation of CO, butane, buta-1,3-diene and furan. As an example, fig. 7 shows the relationship between TOF and N for CO oxidation on  $V_2O_5/TiO_2$  catalysts.<sup>5a</sup> As shown, TOF for CO oxidation and  $S_p$  for toluene oxidation change similarly with respect to the change in N. This is consistent with the idea that surface defects such as steps, kinks or vacancies

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**Fig. 7.** Relationship between the turnover frequency (TOF) and the number of  $V_2O_5$  layers for the CO oxidation.  $\bigcirc$ ,  $V_2O_5/\text{TiO}_2$  (anatase);  $\triangle$ ,  $V_2O_5\text{TiO}_2$  (rutile);  $\diamondsuit$ ,  $V_2O_5$ -U. Reaction temperature = 673 K,  $P_{\text{co}} = 0.045$  atm,  $P_0 = 0.752$  atm.



Fig. 8. Interactions of the toluene molecule with the smooth (010) plane (a) and the step site (b) on  $V_2O_5$ .

are responsible for the selective oxidation of toluene. According to Vejux and Courtine,<sup>15</sup> there is a remarkable fit of the crystallographic patterns between the (010) plane of  $V_2O_5$  and the TiO<sub>2</sub> surface. It is therefore considered that a smooth  $V_2O_5$  surface with few defects is formed for the  $V_2O_5/TiO_2$  catalysts having small N, and that the number of surface defects increases with N. The relationship between  $S_p$  and N is also consistent with this idea.

Since the publication of our papers about the structures of supported vanadium oxides, several important studies have been made into the characterization of supported vanadium oxides, especially regarding the monolayer catalysts.<sup>16,17</sup> It has been shown that the two-dimensional arrangement of vanadium and oxide ions in the monolayer catalyst is very different from that in crystalline  $V_2O_5$ . Since the monolayer catalyst leads to total oxidation to oxides of carbon (fig. 5), this suggests that  $V_2O_5$  layers with surface defects provide active sites for the selective oxidation of toluene. A possible model of the active site for the selective oxidation is shown in fig. 8(b). Note also that one heterogeneity in  $V_2O_5$  layers above the monolayer coverage is taken into account as the distribution of the number of  $V_2O_5$  layers (table 2) and is shown in fig. 5 and 6 as error bars in N.

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### Toluene Oxidation on Vanadium Oxide Catalysts

## Possible Mechanisms for Toluene Oxidation

According to the characterization of vanadium oxide catalysts,<sup>4, 10</sup> there are acidic sites, mainly Brønsted-acid sites, adjacent to surface V=O species. According to quantumchemical calculations similar to those described previously.<sup>14b, 18</sup> the  $\pi$ -electrons of the benzene ring of toluene interact with the acid site to activate the hydrogen atoms of the methyl group in toluene. As discussed above, the abstraction of an H atom of the methyl group by a V=O species is considered to be the rate-determining step of the reaction under excess oxygen conditions. If further reaction of the unstable intermediate species with V=O species is limited in the methy group, selective oxidation to benzaldehyde [the initial product in the reaction path of eqn (2)] would be realized. If the reaction of the intermediate species with V=O species also occurs in the benzene ring of the toluene molecule, the oxidative decomposition to oxides of carbon [eqn (3)] would take place.

Fig. 8 shows possible interactions of the toluene molecule with the smooth (010) plane (a) and a step site (b). From the models, the intermediate species on the smooth (010)plane is considered to have more rotational freedom parallel to the catalyst surface that on the step site. This is consistent with recent observations that the step site plays a role in fixing a special geometry of the adsorbed molecule which cannot be formed on low-Miller-index planes.<sup>19</sup> The larger freedom in the two-dimensional motion on the surface without many defects would lead to a higher probability for the reaction of surface V=O species with the intermediate species at the benzene ring. This in turn may bring about the total oxidation to oxides of carbon. On the step site, on the other hand, the geometry of the intermediate species may be fixed to limit the reaction at the methyl group of toluene. From the stoichiometry of the oxidation of toluene to benzaldehyde,

$$C_6H_5CH_3 + O_2 \rightarrow C_6H_5CHO + H_2O$$

this should be followed by the abstraction of another hydrogen atom and the donation of one oxygen atom to the intermediate species. On the catalysts with V<sub>2</sub>O<sub>5</sub> layers, oxygen atoms necessary for these processes can be supplied from the catalyst bulk without any significant change in the geometry of the intermediate species because the reduced  $V^{4+}$  ion can be reoxidized by bulk oxygen to reproduce the surface V=O species. On the monolayer vanadium oxide catalysts, however, these processes cannot be realized without the transfer of the intermediate species to another V=O species because of the absence of bulk V=O species. This explains the low value of  $S_p$  for the monolayer catalyst. Although a number of alternative mechanisms may be proposed for the role of surface defects on selectivity, the abovementioned mechanism provides a possible interpretation of the observed structure-selectivity/activity correlation for toluene oxidation.

In this study of the oxidation of toluene on well characterized vanadium oxide catalysts, we have found a new type of structure-selectivity correlation which has not previously been observed for the oxidation of benzene, but-1-ene, buta-1,3-diene and furan.<sup>5</sup> Since many interesting studies have been made on the selective oxidation of oxylene on monolayer  $V_2O_5/TiO_2$  catalysts,<sup>17</sup> this reaction seems to provide important information to apply in our approach to the catalysis of vanadium oxides.

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