

## Hexagonal Orthovanadates as Catalysts in the Oxidation of Methanol to Formaldehyde

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Improved selectivities are obtained in the catalytic oxidation of methanol to formaldehyde using hexagonal orthovanadates of the type  $\text{Sr}_{3-x}\text{La}_{2x/3}(\text{VO}_4)_2$  ( $x = 0.3\text{--}1.5$ ) in comparison with those using the strontium and lanthanum orthovanadates separately.

Strontium hypovanadates with the perovskite structure have been tested as catalysts in the oxidation of methanol and benzene, and in anodic oxidations.<sup>1,2</sup> Also, several Sn, Pb, and Bi unsupported and supported vanadates have been used in the catalytic oxidation of *o*-xylene.<sup>3</sup> Transition metal and Sb vanadates were also studied in the catalytic oxidation of methanol.<sup>4,5</sup> However, systematic investigations on the catalytic behaviour of hexagonal orthovanadates of the type  $\text{Sr}_{3-x}\text{La}_{2x/3}(\text{VO}_4)_2$  ( $x = 0\text{--}3$ ) have not been published yet.

Here, we report our initial studies involving the preparation, activities, and selectivities (for formaldehyde formation) of the title compounds which provide catalysts with significantly improved selectivities when compared with those of the strontium and lanthanum orthovanadates tested separately.

The samples of  $\text{Sr}_{3-x}\text{La}_{2x/3}(\text{VO}_4)_2$  were prepared by

reaction of  $\text{V}_2\text{O}_3$  with mixtures of the corresponding metal carbonates at 1173 K for 12 h until  $\text{CO}_2$  removal.<sup>6</sup> Also,  $\text{Sr}_3(\text{VO}_4)_2$ ,  $\text{LaVO}_4$ , and  $\text{La}_2\text{O}_3$  were tested for their catalytic activities, as reference materials. In a typical experiment the catalyst (1 g) was placed in a fixed bed flow reactor of internal diameter 9 mm. Methanol oxidation was performed at 573 K and 1 atm, using air (molar ratio,  $\text{MeOH}:\text{O}_2:\text{N}_2$ , 1:1.5:7.5) at an hourly space velocity of  $1500\text{ h}^{-1}$ . Formaldehyde and unchanged methanol were collected in a trap held at 78 K. Residual  $\text{CO}_2$  gas was analysed by the standard baryta method, while methanol and formaldehyde were analysed spectrophotometrically.<sup>7</sup> Standard analyses of vanadium, strontium, and lanthanum confirm the formula proposed for the catalysts, and powder X-ray diffraction indicates that all compounds ( $x = 0.3\text{--}1.5$ ) show isostructural hexagonal

**Table 1.** Methanol oxidation using the  $\text{Sr}_{3-x}\text{La}_{2x/3}(\text{VO}_4)_2$  catalysts.<sup>a</sup>

$x$	$\text{Sr}_{3-x}\text{La}_{2x/3}(\text{VO}_4)_2$ catalyst	% MeOH conversion	% Selectivity
	Wt. % Sr		
0	53.2	0	0
0.3	47.8	96	7
0.6	42.4	65	11
0.9	37.0	18	19
1.1	33.4	12	78
1.2	31.6	15	8
1.5	26.2	51	6
3	—	60	3
— <sup>b</sup>	—	99	0

<sup>a</sup> Conditions: 573 K; 1 atm; molar ratio  $\text{MeOH}:\text{O}_2:\text{N}_2$  in feed 1:1.5:7.5; space velocity  $1500\text{ h}^{-1}$ . <sup>b</sup>  $\text{La}_2\text{O}_3$  catalyst.

packing of the type in  $\text{Sr}_3(\text{VO}_4)_2$ ,  $d = 3.10$  (s),  $2.81$  (s),  $2.08$  (m),  $1.86$  (m-w),  $1.67$  (m-w),  $1.62$  (w), and  $1.55$  (w) Å, with a fixed oxidation state of  $\text{V}^{5+}$ . The presence of vacancies and defects in the structures would thus be expected.

Table 1 shows the expected inverse relationship between % conversion (mass of MeOH reacted  $\times 100/\text{mass MeOH fed}$ )

and % selectivity (mass of MeOH converted into  $\text{HCHO} \times 100/\text{mass of MeOH converted into HCHO} + \text{CO}_2$ ), and also a drastic increase in selectivity for low conversions, reaching 78% selectivity in the vicinity of  $x = 1.1$ . These results are of significant value when compared with selectivity values of 0 and 3% obtained for  $\text{Sr}_3(\text{VO}_4)_2$  and  $\text{LaVO}_4$  respectively. The amount and distribution of crystal vacancies might well account for the differences observed. These compounds are being further characterised in order to elucidate the nature of the active sites involved.

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