Hexagonal Orthovanadates as Catalysts in the Oxidation of Methanol to Formaldehyde

Pilar Salagre and Jesús E. Sueiras*

Facultat Química, Universitat Barcelona, Pl. Imperial Tarraco, 1, 43005 Tarragona, Spain

Improved selectivities are obtained in the catalytic oxidation of methanol to formaldehyde using hexagonal orthovanadates of the type $Sr_{3-x}La_{2x/3}(VO_4)_2$ (x = 0.3—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.[1,2] Also, several Sn, Pb, and Bi unsupported and supported vanadates have been used in the catalytic oxidation of o-xylene.[3] Transition metal and Sb vanadates were also studied in the catalytic oxidation of methanol.[4,5] However, systematic investigations on the catalytic behaviour of hexagonal orthovanadates of the type $Sr_{3-x}La_{2x/3}(VO_4)_2$ (x = 0—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 $Sr_{3-x}La_{2x/3}(VO_4)_2$ were prepared by reaction of V_2O_3 with mixtures of the corresponding metal carbonates at 1173 K for 12 h until CO_2 removal.[6] Also, $Sr_3(VO_4)_2$, $LaVO_4$, and La_2O_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, MeOH : O_2 : N_2, 1 : 1.5 : 7.5) at an hourly space velocity of 1500 h⁻¹. Formaldehyde and unchanged methanol were collected in a trap held at 78 K. Residual CO_2 gas was analysed by the standard baryta method, while methanol and formaldehyde were analysed spectrophotometrically.[7] 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—1.5) show isostructural hexagonal

Table 1. Methanol oxidation using the $Sr_{3-x}La_{2x/3}(VO_4)_2$ catalysts.[a]

$Sr_{3-x}La_{2x/3}(VO_4)_2$ catalyst		% MeOH conversion	% Selectivity
x	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
—[b]	—	99	0

[a] Conditions: 573 K; 1 atm; molar ratio $MeOH:O_2:N_2$ in feed 1:1.5:7.5; space velocity 1500 h^{-1}. [b] La_2O_3 catalyst.

packing of the type in $Sr_3(VO_4)_2$, 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 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 ×100/mass MeOH fed) and % selectivity (mass of MeOH converted into HCHO ×100/mass of MeOH converted into HCHO + 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 $Sr_3(VO_4)_2$ and $LaVO_4$ 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.

References

1 K. S. De and M. R. Balasubramanian, *J. Catal.*, 1983, **81**, 482.
2 Y. Matsumoto, H. Yoneyama, and H. Tamura, *J. Electroanal. Chem.*, 1977, **79**, 319.
3 K. P. Srivastova and I. K. Yain, *Indian J. Technol.*, 1983, **21**, 155.
4 L. N. Kurina and L. M. Totolytsyna, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 1983, **26**, 1218.
5 M. Romon, A. Masamichi, and E. Etsuro, *J. Catal.*, 1976, **44**, 101.
6 V. L. Volkov and A. K. Slepukhin, *Zh. Neorg. Khim.*, 1977, **22**, 783.
7 'Official Methods of Analysis,' Association of Official Analytical Chemists, Box 540, Benjamin Franklin Station, Washington DC 20044, U.S.A., 1980, p. 156.