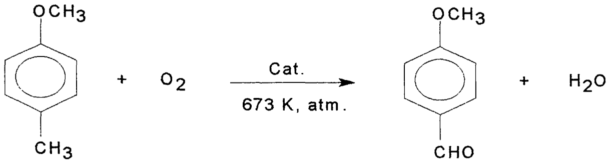
Vapour-Phase Selective Oxidation of 4-Methylanisole to Anisaldehyde over V_2O_5/Ga_2O_3-TiO_2 Catalyst

Benjaram M. Reddy,* Ibram Ganesh, and Biswajit Chowdhury
Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad-500 007, India

(Received July 18, 1997; CL-970566)

The vapour phase partial oxidation of 4-methylanisole to *p*-anisaldehyde was investigated over binary oxide supported vanadium oxide catalysts at 623-748 K under normal atmospheric pressure. Among various catalysts the V_2O_5/Ga_2O_3-TiO_2 effectively performed this reaction with high activity and selectivity.

Anisaldehyde (4-methoxybenzaldehyde) is an important chemical and chemical intermediate having many potential applications. It is used as a perfumer, brightener in plating, and raw material for preparation of pharmaceuticals and agrochemicals. It is a well established fact in the literature that substituted benzaldehydes can be prepared from the corresponding substituted toluenes in liquid phase in the presence of Co, Mn, and Ce salts in acetic acid medium or by electrochemical methods.[1-3] However, efficiencies of these routes are not so high and also produce more wasteful products causing environmental problems. In fact, there are several advantages for carrying out this reaction in the vapour phase.



Therefore, the vapour phase route employing an appropriate heterogeneous catalyst system is preferred over the conventional liquid phase method. However, such attempts are very limited in the open literature.[4-5] For carrying out this reaction in vapour phase, Seko *et al.*[6] used a V_2O_5-P_2O_5-K_2SO_4 catalyst system. Recently, Ueshima and Saito[7] reported 63 % yield of *p*-anisaldehyde over V_2O_5-Tl_2O catalyst at 703 K. Their study[7] further suggested that a well balanced combination catalyst consisting of an acidic oxide such as V_2O_5 and a basic oxide like Tl_2O is very effective for this reaction. However, the use of Tl_2O as a catalytic material in fine chemicals synthesis is restricted in view of its toxic nature.

In this communication we report an efficient Ga_2O_3-TiO_2 mixed oxide supported vanadium oxide catalyst for the title reaction. Mixed oxide supports have attracted the attention recently because of their better performance than their constituent single oxide components in various reactions.[8-10] Since, the physicochemical properties of mixed oxides can be designed more precisely by selecting the concentration of individual components and also by changing the preparative procedures, there is a great scope for several applications. For the purpose of comparison various other mixed oxides *viz.* TiO_2-SiO_2, TiO_2-Al_2O_3, TiO_2-ZrO_2 and TiO_2-SiO_2-ZrO_2 impregnated with vanadium oxide have also been employed in this investigation.

The Ga_2O_3-TiO_2 (1:5 mole ratio) mixed oxide was prepared by a homogeneous precipitation method using urea as hydrolysing agent. The cold titanium tetrachloride (Fluka, AR grade) was first digested in cold concentrated HCl and subsequently diluted with deionized water and to which the Ga_2O_3 (Alchem, GR grade) dissolved in concentrated HCl was added. To this mixed aqueous solution, an excess amount of urea (Loba-Chemie, GR grade) was added and heated to 373 K with vigorous stirring. In about 6 h of heating the formation of precipitate was occurred and the obtained precipitate was heated for six more hours to facilitate ageing. The coprecipitate thus obtained was filtered off and washed thoroughly with doubly distilled water until no chloride ions could be detected. Thus, obtained cake was oven dried at 393 K for 16 h and calcined at 773 K for 6 h in an open air atmosphere. The obtained Ga_2O_3-TiO_2 mixed oxide support had a N_2 BET surface area of 122 $m^{-2}g^{-1}$. To make a monolayer V_2O_5/Ga_2O_3-TiO_2 catalyst, 12 wt% V_2O_5 was impregnated on the support from ammonium metavanadate (Fluka, AR grade) dissolved in 2 M oxalic acid solution. The impregnated sample was oven dried at 393 K for 16 h and calcined at 773 K for 6 h in oxygen atmosphere. More details on the preparation of other mixed oxide supports and vanadium oxide containing catalysts are described elsewhere.[11,12] Catalytic tests were conducted on a fixed-bed micro-reactor system at atmospheric pressure. For each run about 2 g catalyst sample was used, and the reaction products were analysed quantitatively by gas chromatography and qualitatively by NMR spectroscopy. The 4-methylanisole was fed with a metering pump at a rate of 1.5 to 3.0 $cm^3\ h^{-1}$ and dry air was used as source of O_2 and passed at a flow rate of 45 $cm^3\ min^{-1}$. Conversion and product selectivities are calculated as follows:

Conversion (%) = 100 × Number of moles of 4-methylanisole reacted / Number of moles of 4-methylanisole fed.

Selectivity (%) = 100 × Number of moles of *p*-anisaldehyde formed / Number of moles of 4-methylanisole reacted.

The BET surface areas of the catalysts were determined by volumetric N_2 adsorption at 77 K on a conventional all glass high vacuum system. The X-ray powder diffraction measurements were made on a Philips PW 1051 instrument with Ni-filtered CuK_α radiation.

The reaction was investigated between 623 to 723 K temperature. In general an increase in the conversion with an increase in temperature was noted. However, the product selectivity was decreased beyond 673 K with increase in temperature. No appreciable change in the conversion and product selectivity was observed on V_2O_5/Ga_2O_3-TiO_2 catalyst up to 16 h time on stream. For the purpose of better comparison the activity and selectivity results obtained at 673 K are presented in Table 1. The main reaction products analysed are *p*-anisaldehyde (B), *p*-anisic acid (A), and some traces of unknown products including CO and CO_2 (U).

Table 1. The conversion of 4-methylanisole to *p*-anisaldehyde on various mixed oxide catalysts.

Catalyst[a]	BET SA	Conversion	Selectivity (%)		
	(m^2 g^{-1})	(%)	B	A	U
15 V_2O_5/TiO_2-SiO_2	151	40	6	85	9
12 V_2O_5/TiO_2-Al_2O_3	97	44	20	75	5
12 V_2O_5/TiO_2-ZrO_2	108	43	30	62	8
20 V_2O_5/TiO_2-SiO_2-ZrO_2	220	17	21	73	6
12 V_2O_5/Ga_2O_3-TiO_2	55	72	90	4	6

[a] The numbers before V_2O_5 represent the wt.% of V_2O_5. The support composition is 1:1 mole ratio of oxides except Ga_2O_3-TiO_2 (1:5).

The X-ray diffraction studies showed that V_2O_5/Ga_2O_3-TiO_2 is in amorphous state in line with other mixed oxide catalysts. However, ammonia uptake measurements[13] revealed that other catalysts are more acidic than V_2O_5/Ga_2O_3-TiO_2. It is known that vanadium oxide is a well established catalyst for oxidation, ammoxidation and De-NO_x reactions exhibiting the redox properties.[14] Surface acidity and basicity measurements on oxide catalysts have received considerable attention in recent years since they play an important role in the selective oxidation of hydrocarbons.[15-17] Catalytic activity has been closely related to the acidity and basicity of binary oxides.[18,19] Recent studies have shown that there exists a correlation between the oxygen mobility and the basicity of the oxide when used as a support.[20] In the present case the acid-base properties of the support coupled with the redox characteristics of vanadium oxide appears to be responsible for the observed high conversion and product selectivity. As pointed out by Ueshima and Saito[7], for an efficient catalyst, in terms of good conversion and product selectivity, both acid and base functions of the catalyst are necessary.

It is clear that V_2O_5/Ga_2O_3-TiO_2 is an efficient catalyst for the selective oxidation of 4-methylanisole to *p*-anisaldehyde with sufficiently high catalyst life. Studies on the reaction mechanism, and the origin of acid-base properties coupled with redox characteristics of the catalyst are under active progress.

References

1 T. Tzedakis and A.J. Savall, *Ind. Eng. Chem. Res.*, **31**, 2475 (1992); References therein.
2 M. Costantini, L. Dominique, and E. Fache, EP 577,476 (1992); *Chem. Abstr.*, **120**, 191334r (1994).
3 F. Yatsuhoshi, K. Niiyama, M. Ono, and N. Kanada, JP 0499887 (1992); *Chem. Abstr.*,**117**, 57714z (1992).
4 N. Kishimoto, I. Nakamura, T. Matsueda, and Y. Arita, EP 459,729 (1991); *Chem. Abstr.*,**116**, 105844v (1992).
5 I. Nakamura, N. Saito, and M. Ueshima, Jpn. Kokai, JP 6178744 (1986); *Chem. Abstr.*, **105**, 114734j (1986).
6 H. Seko, Y. Tokuda, and M. Matsuoka, *Nippon Kagaku Kaishi*, **1979**, 558.
7 M. Ueshima, and N. Saito, *Chem. Lett.*, **1992**, 1.
8 K.R.P. Sabu, K.V.C. Rao, and C.G.R. Nair, *Bull.Chem. Soc. Jpn.*, **64**, 1920 (1991).
9 B.M. Reddy, E.P. Reddy, and B. Manohar, *Appl.Catal.*, **55**, L1 (1993).
10 B.M. Reddy, I. Ganesh, and E.P. Reddy, *J. Phys. Chem.*, **101**, 1769 (1997).
11 B.M. Reddy, S.S. Madhavendra, and E.P. Reddy, *Indian J. Chem.Technol.*, **1**, 60 (1994).
12 B.M. Reddy, B. Manohar, and S. Mehdi, *J. Solid State Chem.*, **97**, 233 (1992).
13 B.N. Reddy, B.M. Reddy, and M. Subrahmanyam, *J. Chem. Soc., Faraday Trans.*, **87**, 1649 (1991).
14 P. Mars and D.W. van Krevelen, *Chem. Eng. Sci. (Special Suppl.)*, **3**, 41 (1954).
15 H.H. Kung, *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 171 (1992).
16 J. Kijenski and A. Baiker, *Catal. Today*, **5**, 1 (1989).
17 M. Ai, *J. Mol. Catal. A: General*, **114**, 3 (1996); References therein.
18 K. Tanabe, T. Shibata, and J. Kitagawa, *Bull. Chem. Soc. Jpn.*, **47**, 1064 (1974).
19 T. Jin, H. Hattori, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **55**, 2279 (1982).
20 D. Martin and D. Duprez, *J. Phys. Chem.*,**100**, 9429 (1996).