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Catalytic vapor-phase oxidation of 2,2,2-trifluoroethanol

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Abstract

The synthesis of trifluoroacetaldehyde by vapor-phase oxidation of 2,2,2-trifluoroethanol using supported vanadium catalysts was studied. Significant differences were observed in the reaction outcomes resulting from different types of catalysts. The ZrO_2 - and Al_2O_3 -supported catalyst demonstrated both high catalytic activity and selectivity. The addition of co-catalysts such as MoO₃ or SnO₂ improved catalytic performance (Selectivity: up to 91%; S.T.Y.: >200 g L⁻¹ h⁻¹). The experimental results on catalyst lifetime showed a marked decrease in the activity of the Al_2O_3 -supported catalyst within tens of hours, while the ZrO_2 -supported catalyst showed little, if any, performance alterations for 2000 h. © 2006 Elsevier B.V. All rights reserved.

Keywords: Vapor-phase oxidation; 2,2,2-Trifluoroethanol; Trifluoroacetaldehyde; Vanadium oxide

1. Introduction

Recently, the peculiar properties of fluorine have gained wide industrial interest in various fields, including the pharmaceutical, agricultural chemical and electronic materials fields, and fluorine has been incorporated into various functional organic molecules. One of the practical methods of incorporating fluorine into organic compounds is the conversion of building block molecules containing fluorine into target compounds. Trifluoroacetaldehyde **2**, which possesses a simple chemical structure and a highly reactive aldehyde group, is one of the widely applicable building blocks containing fluorine. In addition, utilizing its pro-chiral property, the synthesis of CF_3 -containing chiral compounds has also been explored [1–4].

For the synthetic methods of trifluoroacetaldehyde **2**, several kinds of procedures are known. Fluorination of trichloroacetaldehyde in the vapor-phase [5], reduction of trifluoroacetic acid or its esters in the vapor- or liquid-phase [6,7], and oxidation of trifluoroethanol **1** [8] are among the major conventional methods. In the method of oxidation for trifluoroethanol **1** (Scheme 1), by-products of which separation is difficult aren't generated, unlike in the case of the fluorination reaction in the vapor-phase (which prone to produce incomplete fluorinated compounds) [5]. Also in this oxidation method, compared with the method of reduction of trifluoroacetic acid (which combines

easily with the products forming azeotropic liquids), the separation and recycling of trifluoroethanol, the raw material, is easier. So, utilizing this oxidation method a simplified and advantageous process can be created.

For a large-scale industrial production of trifluoroacetaldehyde **2** using the method of oxidation of trifluoroethanol **1**, the vapor-phase continuous reaction is appropriate. The vapor-phase oxidation reaction has been long studied in the petrochemical industry, but the reported cases of its application to fluorinecontaining compounds are extremely rare. One of the causes thereof is that, in the case of compounds containing fluorine, the electron density of the adjacent portion is low and the oxidation reaction is not easy [9–11] due to the electronegativity of fluorine. Regarding the vapor-phase oxidation reaction of trifluoroethanol **1**, there is a report about the supported V₂O₅ catalyst [8]. Even when 100% oxygen is used as the oxidizer, the raw material conversion rate is as low as 18–41%.

This study investigated the most appropriate type of catalyst for use in the vapor-phase oxidation of trifluoroethanol **1** from the viewpoint of industrial production.

2. Results and discussion

2.1. Catalyst screening

The vapor-phase oxidation reactions of trifluoroethanol 1, using various types of supported V_2O_5 (7 wt.%) catalysts, were studied. The investigation was carried out under conditions of

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Scheme 1.

excess air, with the concentration of trifluoroethanol 1 being controlled under the explosive limit (5.5 vol.%), using air as an oxidizer. The generated trifluoroacetaldehyde 2 was collected in water as hydrate 4 for analysis.

Marked differences in reaction results were observed due to the differences in the chemical formulations of the supports (Table 1). The SiO₂-supported catalyst manifested a low activity, while the Al₂O₃-supported catalyst and the ZrO₂-supported catalyst gave good results for both catalytic activity and selectivity over a wide range of surface area. The TiO₂ (anatase

Table 1 The influence of supports

type)-supported catalyst showed the highest catalytic activity, though it produced trifluoroacetic acid 3 in large proportion.

The differing degree of dispersion of V_2O_5 and its interaction with the support, which resulted from the difference in the support chemical formulations, presumably caused varied effects on the oxidation reaction of trifluoroethanol **1**. The SiO₂-supported catalyst has been reported to have larger particles of V_2O_5 [12]. On the other hand, the TiO₂ (anatase type)-supported catalyst that showed high activity has been reported to have V_2O_5 in a highly dispersed and stratified

Entry	Catalyst	Support		Conversion ^a (%)	Selectivity ^b (%)		S.T.Y. ^c (g $L^{-1} h^{-1}$)
		Name	Surface area (m ² /g)		4	3	
1	V ₂ O ₅ /SiO ₂ ^d	Q-50	80	12	40	Trace	20
2	$V_2O_5/Al_2O_3^e$	SA3135	13	38	92	Trace	156
3	$V_2O_5/Al_2O_3^e$	SA3177	116	51	67	Trace	152
4	$V_2O_5/Al_2O_3^e$	KHO24	140	64	84	Trace	241
5	V_2O_5/ZrO_2^d	XZ16075	53	67	83	7.8	249
6	V_2O_5/ZrO_2^d	XZ16052	95	62	82	5.9	226
7	V_2O_5/ZrO_2^d	XZ16154	258	68	69	Trace	211
8	V ₂ O ₅ /TiO ₂ ^d	CS-300S	69	94	44	41	202

^a The conversion rate was calculated from the quantitative values (the internal reference method) in **1** according to ¹⁹F NMR.

^b The selectivity was calculated from the quantitative values (the internal reference method) in 3 and 4 according to ¹⁹F NMR.

^c S.T.Y. (space time yield) was calculated using the following formula. S.T.Y. = (production weight of 4 per hour: gh^{-1})/(catalyst volume: L).

^d The catalyst was prepared by method A.

^e The catalyst was prepared by method B.

Table 2

The influence of co-catalysts

Entry	Catalyst	Support	Conversion ^a (%)	Selectivity ^b (%)		S.T.Y. ^c (g $L^{-1} h^{-1}$)
				4	3	
1	$V_2O_5/Al_2O_3^d$	KHO24	64	84	Trace	241
2	$V_2O_5 - MoO_3/Al_2O_3^{d}$ (Mo/V = 1.0)	KHO24	54	91	1.8	219
3	$V_2O_5 - SnO_2/Al_2O_3^{d}$ (Sn/V = 1.0)	KHO24	97	84	6.4	369
4	V_2O_5/ZrO_2^e	XZ16052	62	82	5.9	226
5	$V_2O_5 - MoO_3/ZrO_2^{e}$ (Mo/V = 1.0)	XZ16052	63	87	9.1	246
6	$V_2O_5 - WO_3/ZrO_2^{e}$ (W/V = 1.0)	XZ16052	72	80	6.9	254
7	V_2O_5 -TiO ₂ /ZrO ₂ ^d (Ti/V = 0.5)	XZ16052	74	85	5.8	278
8	$V_2O_5 - SnO_2/ZrO_2^{d}$ (Sn/V = 1.0)	XZ16052	80	82	7.7	293
9	V_2O_5/ZrO_2^e	XZ16075	67	83	7.8	249
10	$V_2O_5 - MoO_3/ZrO_2^e$ (Mo/V = 1.0)	XZ16075	64	91	7.0	257
11	$V_2O_5 - SnO_2/ZrO_2^{d}$ (Sn/V = 1.0)	XZ16075	85	80	15	305

^a The conversion rate was calculated from the quantitative values (the internal reference method) in 1 according to ¹⁹F NMR.

^b The selectivity was calculated from the quantitative values (the internal reference method) in 3 and 4 according to ¹⁹F NMR.

^c S.T.Y. (space time yield) was calculated using the following formula. S.T.Y. = (production weight of 4 per hour: gh^{-1})/(catalyst volume: L).

^d The catalyst was prepared by method B.

^e The catalyst was prepared by method A.

manner through crystallographic conformity between V_2O_5 (0 1 0) plane and TiO₂ surface [13].

Next, the effect of co-catalyst metals was studied with regard to the Al_2O_3 -supported catalyst and the ZrO_2 -supported catalyst (Table 2). Both catalysts showed enhanced selectivity of trifluoroacetaldehyde hydrate **4** due to the addition of MoO₃, and increased catalytic activity due to the addition of SnO₂. The addition of WO₃ or TiO₂ also resulted in enhanced catalytic activity.

The effects of the addition of these co-catalysts are also reported for the vapor-phase partial oxidation reaction of unfluorinated compounds (benzene [14], xylene [15], etc.). The addition of other kinds of metal oxides such as MoO_3 is speculated to produce compound oxides [16], which affected the reactions.

Since the catalytic site of the V₂O₅ oxidation reaction is considered to be the double-bonded oxygen of V=O [12], the V=O bonding status was investigated by measuring the infrared absorption spectrum (Fig. 1). The results indicated absorption at 1009 cm⁻¹ for the V₂O₅/ZrO₂ catalyst, which corresponded to the V=O stretching vibration, a shift toward a lower wavenumber than that of unsupported V₂O₅ (1026 cm⁻¹). Furthermore, the V₂O₅–SnO₂/ZrO₂ catalyst which exhibited higher catalyst activity showed absorption at 986 cm⁻¹ for the V=O stretching vibration. These results suggested that the supports and co-catalysts contributed to weakening the V=O bonding strength by interacting with V₂O₅, which facilitated the oxidation process.



Fig. 1. Infrared absorption spectra of catalyst: (a) V_2O_5 (not supported); (b) V_2O_5/ZrO_2 (XZ16052); (c) V_2O_5 -SnO₂/ZrO₂ (XZ16052).



Fig. 2. Catalyst lifetime test: (\bigcirc) V₂O₅–SnO₂/Al₂O₃ (KHO24); (\blacksquare) V₂O₅–SnO₂/ZrO₂ (XZ16075); (\blacktriangle) V₂O₅–MoO₃/ZrO₂ (XZ16052); temperature: 260–280 °C; catalyst: 20 mL; reaction tube diameter: 15 mm; concentration of 1: 2.2 vol.%; space velocity: 4300 h⁻¹ (flow rate: L h⁻¹/catalyst volume: L).

2.2. Catalyst lifetime

Catalyst lifetime was examined through continuous reactions by using the V₂O₅–SnO₂/Al₂O₃, V₂O₅–MoO₃/ZrO₂ and V₂O₅–SnO₂/ZrO₂ catalysts which showed high performance through catalyst screening (Fig. 2). The results indicated that the V₂O₅–MoO₃/ZrO₂ and V₂O₅–SnO₂/ZrO₂ catalyst maintained catalyst performance for over 100 h. On the other hand, the V₂O₅–SnO₂/Al₂O₃ catalyst decreased the yield of trifluoroacetaldehyde hydrate **4** as the reaction continued.

To search for the underlying causes, we analyzed the retrieved catalysts (Table 3). The results of X-ray fluorescence analysis revealed no compositional changes in the V_2O_5 -MoO₃/ZrO₂ catalyst, but showed a large increase in the quantity of fluorine in the V_2O_5 -SnO₂/Al₂O₃ catalyst. This finding leads to a conjecture that the fluorination of the Al₂O₃ support by HF, a by-product generated during the course of the reaction, caused performance changes. In contrast, when ZrO₂ was used as a support, the catalytic performance was maintained without being influenced by the generated by-products.

To further grasp the potential of the V_2O_5 -SnO₂/ZrO₂ catalyst, the temperature of the catalyst layer was increased to 320 °C, and continuous reactions were carried out under conditions of high loading with an elevated conversion rate (Fig. 3). Under these circumstances, the observed sustained

Table 3		
The result of X-ray	fluorescence	analysis

Reaction time (h)	V ₂ O ₅	ZrO_2	MoO ₃	HfO ₂	F (wt.%)			
V ₂ O ₅ -MoO ₃ /ZrO ₂ (XZ16052)								
6	5.9	83.0	9.5	1.6	Not detected			
266	5.8	82.9	9.6	1.7	Not detected			
Reaction time (h)	V_2O_5	A	$_{2}O_{3}$	SnO ₂	F (wt.%)			
V ₂ O ₅ -SnO ₂ /Al ₂ O ₃ (KHO24)								
6	8.8	88	.0	3.2	Not detected			
72	7.6	77	.5	2.4	12.5			



Fig. 3. Lifetime test of V_2O_5 -SnO₂/ZrO₂ (XZ16075) catalyst: (\bigcirc) conversion of 1; (\blacktriangle) selectivity of 4; (\blacksquare) yield of 4; temperature: 290–320 °C; catalyst: 116 mL; reaction tube diameter: 25 mm; concentration of 1: 3.2 vol.%; space velocity: 2900 h⁻¹ (flow rate: L h⁻¹/catalyst volume: L).

performance lasted for 2000 h, indicating a feasibility of industrializing the use of this catalyst.

3. Conclusion

The supported V₂O₅ catalyst produced trifluoroacetaldehyde hydrate **4** with high selectivity in the vapor-phase oxidation of trifluoroethanol **1** with air as the oxidation agent. Co-catalysts and catalyst supports caused transition in the V=O bonding status, which is the catalytic site, exerting a significant effect on the reaction process. The successful oxidation of trifluoroethanol **1** requires a suitable selection of catalyst supports that are inert to fluorination by HF, an unfavorable by-product. The V₂O₅–SnO₂/ZrO₂ catalyst, possessing high catalytic activity and durability, offers good prospects as an efficient industrial catalyst.

4. Experimental

4.1. Materials and apparatus

The Al_2O_3 supports were supplied by Sumitomo Chemicals Co. Ltd. (KHO24) and Saint Gobain NorPro (SA3135, SA3177). The ZrO₂ supports (XZ16052, XZ16075, and XZ16154) were supplied by Saint Gobain NorPro. The SiO₂ support (Q-50) was supplied by Fuji Silysia Chemical Ltd. The TiO₂ support (CS-300S) was supplied by Sakai Chemical Industry Co. Ltd.

 NH_4VO_3 (Wako Pure Chemical Industries), $(NH_4)_6$ $Mo_7O_{24}\cdot 4H_2O$ (Wako Pure Chemical Industries), SnO_2 (Aldrich Company), $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ (Wako Pure Chemical Industries), and TiO₂ (Wako Pure Chemical Industries) were used as the source of V, Mo, Sn, W, and Ti, respectively.

The ¹⁹F NMR spectrum and the infrared absorption spectrum were recorded on the JEOL FX90Q model (84.25 MHz) and Shimadzu FTIR-8100 model, respectively. The X-ray fluorescence analysis was performed on JEOL JSX-3200 model.

4.2. General procedure for preparation of catalyst

Catalysts were prepared according to known methods [17,18].

4.2.1. Method A

 NH_4VO_3 (4.4 g, 0.038 mol) (and co-catalyst metal source) was added to a flask containing pure water (210 g) and dissolved by heating. Then, support (45 g) was added and, after evaporating water while stirring, the mixture was dried at 150–200 °C for 1 h. The obtained catalyst was placed into a stainless steel tube of 15 mm diameter and baked for 3 h at 450–500 °C in an air stream.

4.2.2. Method B

 NH_4VO_3 (4.4 g, 0.038 mol) (and co-catalyst metal source) and oxalic acid (6.8 g, 0.076 mol) were added to a flask with pure water (20 g) in it, and dissolved by reduction. Then, support (45 g) was added and, after evaporating water while stirring, the mixture was dried at 150–200 °C for 1 h. The obtained catalyst was placed into a stainless steel tube of 15 mm diameter and baked for 3 h at 450–500 °C in an air stream.

4.3. General procedure for vapor-phase oxidation

Catalyst (20–24 mL) was placed into a 15 mm diameter stainless steel reaction tube, and three reaction gas absorption containers filled with 200 g of water were connected to the outlet of the reaction tube. After setting the temperature of the catalyst layer to 250–260 °C while in the air stream at 1.4–1.7 L/min, 2,2,2-trifluoroethanol was fed at 0.13–0.16 g/min. The reaction elevated the temperature of the catalyst layer by 10–20 °C.

After doing the reaction for 4 h, the reaction became stabilized. Then the gas absorption containers were replaced and the reaction was continued for another 2 h. The gas absorption liquid obtained for a period of 4-6 h was analyzed by ¹⁹F NMR with acetone-d6 as the solvent and benzotri-fluoride as the internal standard.

4.4. Measurement of infrared absorption spectra

A few catalyst pellets were ground into fine powder and mixed with KBr powder, and then measurements were performed by diffuse reflection spectroscopy.

4.5. X-ray fluorescence analysis

A few catalyst pellets were ground into fine powder and formed into a pellet, and then measurements were performed (Voltage 30 kV; Live time 600 s).

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