

The Selective Dehydrogenation of Ethane over $\text{SnO}_2\text{-P}_2\text{O}_5$ Catalysts

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Ethane undergoes highly selective catalytic oxidative dehydrogenation over $\text{SnO}_2\text{-P}_2\text{O}_5$ catalysts at 823 K and pressures in the range 6.6–26.4 bar.

Commercially, ethane is dehydrogenated to ethene by non-catalytic steam cracking carried out at a temperature of around 1073 K. Few catalytic processes describing the oxidative dehydrogenation have been reported, the best being an 80% conversion into ethene using nitrous oxide over MoO_3 supported on silica gel, but only after 100 minutes reaction in a closed system.¹ Tin(IV)-phosphorus catalysts have been reported to catalyse the conversions of monoalkenes into dialkenes and ethylbenzene into styrene.² In the present work we report the catalytic, highly selective dehydrogenation of ethane over mixed $\text{SnO}_2\text{-P}_2\text{O}_5$ catalysts at moderately high pressures.

The $\text{SnO}_2\text{-P}_2\text{O}_5$ catalysts were prepared by dissolving the appropriate amount of tin(IV) chloride in triply-distilled water to produce about a 4 M solution. After this stage was complete, sufficient phosphoryl chloride was added to the solution to produce a mixture of the desired Sn:P ratio. The resulting solution was brought to pH 4 by the addition of aqueous 0.880 ammonia during which time the solution gelled. The gel was centrifuged, redispersed in water until all chloride was removed, treated with 1 M nitric acid, and dried in air at 120 °C. Catalytic studies were performed using a stainless steel fixed bed flow microreactor capable of operating at pressures up to ca. 30 bar. Runs were carried out using 2 g of catalyst activated by thermal pretreatment for 16 h at 573 K in a stream of air. The gas mixture comprised ethane (40%), oxygen (10), and nitrogen (50), with flow rates through the catalyst bed of

between 6 and 33.3 $\text{cm}^3 \text{s}^{-1}$. Product analysis was by conventional gas chromatography using both hot wire and flame ionisation detection.

The problem usually encountered with catalysts based on tin(IV) oxide is that of exhaustive oxidation of the hydrocarbon to give unacceptably large amounts of the oxides of carbon, CO and CO_2 . For example in the present case, when the ethane- $\text{O}_2\text{-N}_2$ gas mixture was passed through a SnO_2 catalyst at 823 K and 1 atm pressure, the major products were CO_2 and ethene along with smaller amounts of CO and methane. This product distribution was not significantly altered on increase of the applied gas pressure up to 26.4 bar (Table 1). Even greater amounts of CO_2 were obtained using the $\text{SnO}_2\text{-P}_2\text{O}_5$ catalysts with a gas pressure of 1 atm at the same temperature, and further the molar conversions of ethane were greatly reduced. However for these catalysts, when the applied gas pressure was increased, both the molar conversion of ethane and the selectivity towards ethene formation were dramatically increased. Optimum selectivities of >90% were observed with conversions in the range 37.4–64.3% for the catalysts containing a Sn:P ratio of ca. 0.5. Lower selectivities (<80%) were obtained with catalysts containing lower amounts of phosphorus under the same conditions, and at lower catalyst bed temperatures. Typical data are presented in Table 1.

Mechanistically, the production of CO_2 and methane can be rationalised by analogy with our previous i.r. studies on the chemisorption of ethane onto $\text{SnO}_2\text{-SiO}_2$ and Pd-SnO_2 .³ In those cases, we proposed that chemisorption of ethane involved C-H bond fission at adjacent surface oxide sites with the formation of surface hydroxy and surface ethoxide; which then underwent rapid oxidation to surface acetate. Reaction of this surface species with an adjacent surface hydroxy group yields methane and surface bidentate carbonate, which decomposes evolving carbon dioxide. Formation of ethene may either arise from the abstraction of a β -hydrogen atom from a surface ethoxide with simultaneous elimination of an ethene molecule, or by the concerted abstraction of two hydrogen atoms from a physisorbed ethane molecule at two adjacent surface oxide sites. Why the $\text{SnO}_2\text{-P}_2\text{O}_5$ catalysts should enhance the dehydrogenation reaction is as yet not totally understood, but is probably owing to the presence of highly nucleophilic surface phosphorus oxide sites, which would favour hydrogen abstraction.

We acknowledge support from the S.E.R.C. and B.P. (Chemicals) Ltd. for support in the form of a CASE Award (to A. A.).

Received, 3rd April 1986; Com. 437

References

- 1 M. B. Ward, M. J. Lin, and J. H. Lunsford, *J. Catal.*, 1977, **50**, 306.
- 2 S. J. Blunden, P. A. Cusack, and R. A. Hill, 'The Industrial Uses of Tin Chemicals,' The Royal Society of Chemistry, London, 1985.
- 3 P. G. Harrison and B. Maunders, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1311.

Table 1. Conversion and selectivity data for ethane conversion.

Catalyst	Pressure (bar)	Flow rate ($\text{cm}^3 \text{s}^{-1}$)	Conversion (Molar %)	Selectivity (Molar %)			
				CO	CO_2	CH_4	C_2H_4
SnO_2	1.05	6	37.3	6.3	36.8	10.6	46.3
	26.4	6	50.2	10.3	25.2	17.6	46.9
	26.4	33.3	24.9	11.5	14.1	22.0	52.4
$\text{SnO}_2\text{-0.11P}_2\text{O}_5^a$	1.05	6	3.5	—	40.0	—	60.0
	6.6	33.3	40.0	4.7	0.5	14.7	75.9
	13.2	33.3	17.6	—	1.7	18.0	78.7
	19.8	33.3	21.8	3.1	4.8	16.1	73.3
	26.4	33.3	14.5	6.2	8.1	19.4	62.0
$\text{SnO}_2\text{-0.63P}_2\text{O}_5^b$	1.05	6	17.1	—	69.7	—	30.2
	6.6	6	30.4	—	—	15.1	84.6
	13.2	6	64.3	—	2.0	4.6	93.3
	19.8	6	48.8	—	—	6.1	93.9
	26.4	6	27.1	5.2	8.5	10.5	75.7
	6.6	33.3	21.3	—	7.2	12.4	79.7
	13.2	33.3	53.9	—	2.4	4.0	92.0
	19.8	33.3	37.4	—	—	5.6	91.3
	26.4	33.3	48.5	—	1.2	3.5	92.1

^a Surface area after calcination at 573 K for 16 h in air 178 $\text{m}^2 \text{g}^{-1}$.

^b Surface area after calcination at 773 K for 16 h in air 103 $\text{m}^2 \text{g}^{-1}$.