

## Epoxidation of Ethylene over Silver Catalysts modified by Sodium Chloride

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The selectivity of epoxide synthesis in the direct oxidation of ethylene is increased to 85—87% by addition of sodium chloride to the silver catalyst; this selectivity corresponds to the maximum expected by mechanistic studies.

Present silver catalysts for the manufacture of ethylene oxide by the direct oxidation of ethylene convert about 20% of the reacted olefin into combustion products. To achieve high selectivities, besides the addition of one or more alkali or

alkaline earth metals to the catalyst, organic chlorides are included in the reactant gases.<sup>1</sup> In the work reported here, we examined the effects of separate and simultaneous inclusion of sodium and chlorine-containing additives to the silver cata-

**Table 1.** Results on epoxidation of  $C_2H_4$  [catalyst weight used 0.2 g; flow rate 4 ml min<sup>-1</sup> (s.t.p.)].

Catalyst	Catalyst composition <sup>a</sup>	Temperature/°C	Time/min	$X_{et}^b/\%$	$X_{ox}^c/\%$	$S^d/\%$
Ag		170	78	2.55	13.4	64.0
		200	122	8.44	52.1	52.3
		230	101	12.3	90.4	33.0
Ag-Na	1/0.04	230	70	2.12	8.22	78.4
Ag-Cl	1/0.04	270	115	6.30	27.4	73.0
		200	42	5.00	29.3	53.9
Ag-NaCl	1/0.04	230	44	11.8	79.2	42.8
		230	77	0.62	1.59	86.8
Ag-NaCl <sup>e</sup>	1/0.04	270	127	2.31	6.85	85.8
		270	150	2.33	7.23	85.7
Ag-NaCl	1/0.5	270	186	2.36	7.24	87.6
			1017	2.56	8.33	87.5
Ag-NaCl	1/1	270	120	1.93	5.98	86.5

<sup>a</sup> Equivalent ratio of Ag to additive. <sup>b</sup> Total ethylene conversion. <sup>c</sup> Total oxygen conversion. <sup>d</sup> Selectivity to  $C_2H_4O$ . <sup>e</sup> Prepared from  $NaNO_2$  and  $NH_4Cl$ .

lyst; the particular additives were sodium nitrite, ammonium chloride, and sodium chloride. No catalyst support was used. Silver oxide ( $Ag_2O$ ) was mixed with an aqueous solution of the additive, then dried and powdered. The powder was subsequently reduced by exposing it to a stream of hydrogen at 60–200 °C for 10–15 h followed by treatment at 400 °C for a further 3 h. The equivalent weight of additive was generally 0.04 that of the silver catalyst, but, where indicated, certain other proportions were used. The oxidations were performed at atmospheric pressure in a flow reactor using a gas mixture comprising ethylene, oxygen, and nitrogen in the volume proportions 43, 12, and 45. No organic chloride was added to this gas mixture.

Whilst the catalyst prepared by addition of ammonium chloride to silver showed no marked increment in selectivity and whereas that prepared by addition of sodium nitrite showed some increase in selectivity, the catalyst prepared by addition of sodium chloride resulted in very high selectivities (85–87%) albeit at a somewhat lower activity. This effect of sodium chloride was reproduced with a catalyst made by the simultaneous addition of sodium nitrite and ammonium chloride. Ethylene conversion increased linearly with contact time over the range 0.64 to 2.6 g min<sup>-1</sup> (g-mole of ethylene)<sup>-1</sup>, but selectivity remained unchanged. In separate experiments, this ethylene oxidation catalyst was shown to be almost inactive as a catalyst for the combustion of ethylene oxide. These results suggest that ethylene oxidation over the catalyst comprises parallel reactions of epoxidation and combustion of ethylene.

Activities of those catalysts prepared by inclusion of sodium nitrite or ammonium chloride in an equivalent ratio to silver of 0.5 were very low; ethylene conversion at 270 °C being 0.10% and 0.15%, respectively. These findings indicate

that large amounts of sodium added as sodium nitrite, or chlorine added as ammonium chloride strongly deactivate silver catalysts. In contrast addition of sodium chloride itself deactivated the silver rather less; ethylene conversion at 270 °C being 2.36%. Similar activities were observed at both lower and higher equivalent ratios of sodium chloride. The results are summarised in Table 1. In rather more detail, increasing amounts of sodium chloride, whilst slightly reducing reactivity expressed in terms of total catalyst mass, actually increased reactivity when referred solely to weight of silver; selectivity was essentially constant. Following reduction with hydrogen at 400 °C, the sodium chloride doped catalysts were characterised by X-ray diffraction to be a mixture of bulk sodium chloride and metallic silver. Together with the activity and selectivity data, the X-ray diffraction results may be interpreted as indicating that whilst sodium chloride controls the catalytic performance of silver, probably *via* its surface, the bulk of the additive interacts little with the silver. The results obtained here suggest that simultaneous interaction of cations and anions with silver is an effective and important factor in the achievement of the maximum selectivity (85.7%) foreshadowed in the mechanistic proposals of Kilty and Sachtler.<sup>2</sup>

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## References

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