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Polymerisation versus hydrogenation during ethene adsorption on Rh/TiO₂

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Abstract. Adsorption of ethylene on a Rh/TiO₂ catalyst where there are strong metal-support interactions has been studied. Polymerisation has been observed in the absence of H₂, while in the presence of H₂ hydrogenation to ethane is achieved.

The strong metal-support interactions (SMSI) developed in titania-supported noble metals after high-temperature reduction [1] can be explained on the basis of Ti³⁺ formation. Despite this, and the known role played by Ti³⁺ species in polymerisation processes (Ziegler–Natta catalysts), the relationship between such SMSI and the activity of metal–titania systems in polymerisation reactions has not been reported in the literature, and it is the aim of the present paper to rectify this situation.

The catalyst (12.5% Rh w/w) was obtained by impregnation of TiO₂ (Degussa P-25, 50 m² g⁻¹) with a solution of RhCl₃(aq) and reduction in H₂ at 773 K. After oxidation at 773 K three samples were obtained by reducing at 473, 623 or 773 K [2]. The samples were then contacted at room temperature with C₂H₄ or with an equi-molecular mixture of C₂H₄ + H₂; control experiments were performed with the support treated in the same way. Pressure changes were monitored (Baratron MKS) and the gas phase analysed (gas chromatography, Kromatix 2000C, Porapak Q, 2 m × $\frac{1}{8}$ "); XPS spectra were recorded with mass spectrometry (Leybold–Heraeus LHS-10).

After reduction at 473 K the support does not adsorb ethene, while the sample of Rh/TiO₂ gives rise to Langmuir-type adsorption isotherms, with C₂H₄:Rh_{surf} = 1:4 (from the metal dispersion, 46%, measured by hydrogen adsorption), suggesting the formation of ethylidene species. If hydrogen is present, total hydrogenation to ethane is achieved with Rh/TiO₂, while no reaction (hydrogenation or adsorption) with the support is observed.

On reducing in hydrogen at higher temperatures, hydrogenation is observed with Rh/TiO₂ in the presence of H₂, but in the absence of H₂ and for TiO₂ a continuous decrease of the gas-phase pressure is observed in all cases. Mass spectrometry analysis of the desorbed species showed peaks due to C₃H₈⁺ and C₃H₇⁺ species, in addition to those expected for fragments from ethene.

The results for the samples reduced at 623 and 773 K show the adsorption–polymerisation process to take place in two steps—first a fast adsorption, and then a slow adsorption. From a comparison of adsorption capacities (amounts of gas adsorbed

after a given time), the adsorption on Rh/TiO₂ was found to be 30% lower than that on the support reduced in the same conditions.

The amount of Ti³⁺ species formed upon reduction is larger than for the support alone reduced in the same conditions [3], but these species are mainly located under or in the close vicinity of the metallic particles [4]. Adsorption on Rh/TiO₂ is *faster* than on reduced TiO₂, as the presence of the metallic phase speeds the adsorption of the gas, which is then polymerised on the Ti³⁺ species on the surface of the support.

So, it may be concluded that SMSI in Rh/TiO₂ systems lead to polymerisation if hydrogen is absent; this polymerisation proceeds more easily in the presence of the metallic phase—probably because rhodium favours the adsorption and formation of ethylidene species, which are then transferred to the support, where polymerisation takes place on reduced Ti³⁺ sites. Alternatively, if hydrogen is present, these ethylidene species are readily hydrogenated before they are transferred to the support, while on the reduced support polymerisation persists.

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