

The reactive role of CO₂ in reactions with oxygen. Implications on the selectivity.

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Introduction

CO₂ is produced in large amounts in selective oxidation and ammoxidation reactions. CO₂ can act as an oxidant at low temperature [1]. The probable explanation of the oxidant role of CO₂ is that even at low temperature, CO₂ can undergo dissociation on the surface (CO₂ (g) = CO_{ads} + O_{ads}). The formed oxygen species O_{ads} is able to induce a higher oxidation state of metal-containing oxides during the reaction. Activity and selectivity might be extremely dependent on this process. During the reaction, CO₂ succeeds in maintaining the structure of the catalysts in a rather higher oxidized state, even under a reductive atmosphere. This higher oxidation state promotes the formation of CO₂ and then the non-selectivity [1, 2, 3]. In order to design process to improve selectivity when CO₂ is produced during the reaction it is important to understand in detail the parameters and mechanism from which the dissociation of CO₂ depends and the reactivity of the dissociated species.

We present XPS and *operando*-DRIFTS results, investigating the dissociation of CO₂ on Rh supported catalysts. The hydrogenation of CO₂ at low temperature (<150°C) has been used to study the reactivity of the dissociated species. We demonstrate that the dissociation of CO₂ in reaction conditions depends of the nature of the support, of the size of the metallic particles and of the oxidation state of supported metal. These results are useful to control the dissociation of CO₂ in order to depress non-selectivity or, on the contrary, to promote dissociation, when the formation of the selective product needs more oxidized catalysts, then improving selectivity as could be the case in the epoxidation of ethylene and olefins on Ag supported catalysts [4,5].

Experimental

Rh catalysts supported on TiO₂ or γ -Al₂O₃ were prepared by wet impregnation (RhCl₃). Drying at 110°C overnight, calcined at 450°C/4h. Reaction tests were carried out using a fixed bed reactor operated continuously or by sending pulses of gases. The reaction was performed also by *operando*-DRIFTS. Catalysts were characterized by XPS, H₂ and N₂-adsorption.

Results/Discussion

The types of CO adsorption that is coming from a mixture of CO₂ and H₂, are presented in Fig.1. CO adsorption modes depend on the support, when TiO₂ is used as support CO adsorption band appears at 2050 cm⁻¹ which is assigned to CO adsorbed in a linear form over Rh. Another band appears at 1890 cm⁻¹ and can be ascribed to CO adsorbed in a bridged form.

In the case of Rh/ γ -Al₂O₃ catalysts, the CO adsorption band appears at a wavenumber somewhat lower, with two peaks at 2030 and 2040 cm⁻¹. These two peaks can be associated with Rh-CO species. Regarding the stability of these species, Fig.2 shows the evolution of CO adsorbed bands when H₂ is admitted into the DRIFTS cell. In the case of Rh(1%)/TiO₂ catalyst, the CO adsorption band starts to disappear rapidly due to reaction with H₂. On the contrary, the adsorption of CO on Rh(1%)/ γ -Al₂O₃ is stronger, as seen in fig.2 the bands intensity decreases slowly in 50 min.

Above results show that the way CO₂ is dissociated depends of the support. When H₂ is absent CO₂ cannot be dissociated as no band coming from CO species is observed. Results from XPS show that Rh oxidation state varies between γ -Al₂O₃ and TiO₂. Rh supported on TiO₂ is clearly in a more reduced state (Rh⁰ in the surface around 70%) compared to Rh on γ -Al₂O₃ where metallic Rh comprises nearly 40% of surface Rh. Clearly, the state of Rh can influence the adsorptive properties of CO₂ on Rh surfaces. Depending of the oxidation state of Rh, more or less reactive adsorbed species can be formed. Present results can offer guidelines to improve selectivities in gas phase oxidation in which CO₂ plays a non selective role or when the oxidation process needs the presence of more oxidised sites. In addition, it was demonstrated that dissociation depends of the presence of oxygen in the reactant mixtures and that O_{ads} can migrate from one catalytic phase to another.

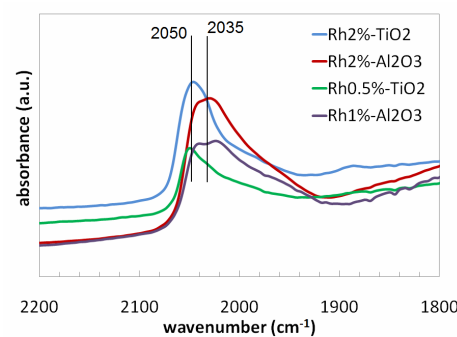


Fig.1: CO adsorption bands from CO₂ dissociation at 150°C in a CO₂ (10%) + H₂ (40%) stream.

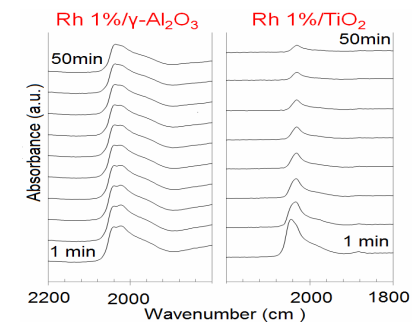


Fig.2: Variation of CO adsorption bands when hydrogenated at 150°C over Rh catalysts.

References.

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