Mechanistic Aspects of CO_2 Hydrogenation at Low Temperature over Rh Catalysts Studied by *Operando*-DRIFTS

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Introduction and Objectives

The transformation of CO_2 in high added-value chemicals to be introduced in chemistry and petrochemical industries is a realistic contribution to the protection of the environment. We have shown previously that on Rh-based catalysts, CO_2 methanation occurs with 100% selectivity and at low temperature (< 200°C) [1, 2]. By *operando*-DRIFTS it was demonstrated that CO_2 is adsorbed dissociatively on Rh, that different CO(ads) species with different reactivity are formed on the surface of the catalyst, that formate species are only spectator during the reaction and that the activation energy of the CO hydrogenation correspond to the same activation energy of the overall CO_2 hydrogenation, supporting the fact that hydrogenation of CO(ads) species could be the rate limiting step of the reaction [3]. In this work we present further results using the same technique which give new insights of the mechanistic aspects of the CO_2 methanation over Rh/TiO_2 and $Rh/\gamma\text{-}Al_2O_3$ catalysts.

Results and Discussion

$Rh/\gamma\text{-}Al_2O_3$ and Rh/TiO_2 catalysts with varying Rh cluster size were using different metal contents. Mean Rh particle sizes were between 1.8 and 17 nm. The activity of the catalysts in CO_2 methanation is shown in Table 1. Catalytic activity increases with Rh particle size and is up to 10 times higher for Rh/TiO_2 catalysts. *Operando*-DRIFTS was used to explain the important differences in activity between catalysts with different particle sizes and supports. XPS complement these results. The interaction of CO_2 + H_2 with the catalyst surface led to the formation of linear CO(ads) species (2040-2050 cm^{-1}) at temperatures as low as 50°C. In the case of large Rh particles, bridge-bonded CO was also detected. In the case of $Rh/\gamma\text{-}Al_2O_3$ catalysts, CO(ads) is associated to hydrogen as Rh carbonyl hydride [3]. The reactivity of surface species was

Table 1. Activity of different Rh catalysts in CO_2 methanation (CO_2/H_2 = 1/4) at 150°C and 1 atm. SV = 100 ml g^{-1} min^{-1}.

Catalyst	Rh particle size (nm)	TOF_{CH4} ($x10^2$) s^{-1}
$Rh(0.5\ wt.\%)/TiO_2$	1.8	0.072
$Rh(1\ wt.\%)/TiO_2$	4.5	0.500
$Rh(3\ wt.\%)/TiO_2$	17.3	2.260
$Rh(1\ wt.\%)/\gamma\text{-}Al_2O_3$	3.6	0.092
$Rh(3\ wt.\%)/\gamma\text{-}Al_2O_3$	15.4	0.333

studied by transient experiments. When the gas feed is changed from CO_2 + H_2 to H_2, CO(ads) bands starts to disappear due to their hydrogenation to form methane. In Figure 1 the comparison of the two supports is presented. In the case of Rh(3 wt.%)/γ-Al_2O_3, the reactivity of CO(ads) band is lower than Rh(3 wt.%)/TiO_2. This stresses the fact that CO(ads) species are the direct precursors of methane over these catalysts, and that the differences in CO_2 methanation activity are related to the differences in the rate of CO(ads) hydrogenation.

Catalysts with different Rh particle sizes show very different behaviour in transient experiments (Figure 2). In the case of catalysts with larger particle sizes (e.g. Rh(3 wt.%)/TiO_2, dp = 17.3) when CO_2 was switched off, the methane formed showed a steady decrease with time. This is explained by the depletion of CO(ads) species from the surface, which is the primary source of methane. In contrast, the behaviour of Rh/TiO_2 catalysts with smaller cluster size (Rh (0.5 wt.%) and Rh(1 wt.%) with Rh cluster sizes of 1.8 and 4.5 nm respectively) is different: After changing from CO_2 + H_2 to H_2, the decrease in CO(ads) peak is accompanied by an increase in methane signal, that is, the production of methane is favoured when CO(ads) coverage is decreased. It is suggested that the supply of hydrogen is more easily performed in Rh/TiO_2.

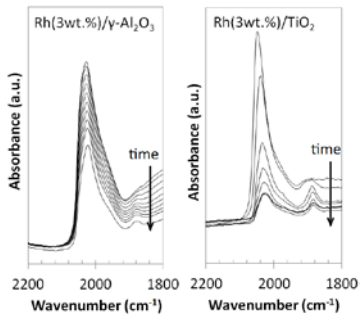

Figure 1: Evolution of CO carbonyl band in transient experiments in H_2 at 150°C Spectra taken with 5 min intervals.

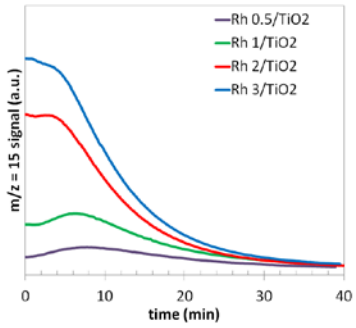

Figure 2: Methane MS signal at the exit of the DRIFTS cell for Rh/TiO_2 with different Rh loading. Transient experiments at 150°C after switching from a CO_2(10%)+ H_2(40%) in He feed to H_2 (40%)/He.

Conclusions

Operando DRIFTS allowed the study of the effect of support and metallic cluster size on the activity of TiO_2 and γ-Al_2O_3-supported Rh catalysts. It was found that smaller Rh clusters are less reactive due to their saturation with CO(ads) species during reaction. TiO_2 was found to be a more effective support than γ-Al_2O_3 which is related to its promoted CO(ads) hydrogenation over this class of catalysts.

References

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[3] A. Karelovic and P. Ruiz, Appl. Catal. B (In Press), DOI: 10.1016/j.apcatb.2011.11.043.