Selective CO₂ methanation on Ru/TiO₂ catalyst: unravelling the decisive role of the TiO₂ crystal structure

<u>Ara Kim</u>^{1,2}, Clément Sanchez, Damien P. Debecker^{1*}, Capucine Sassoye^{2*} ¹Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Croix du Sud, 2/17,1348 Louvain-la-Neuve, Belgium. ² Laboratoire de Chimie de la Matière Condensée de Paris, Collège de France, 11 place Marcelin Berthelot, 75231, Paris cedex 05, France *corresponding author: capucine.sassoye@upmc.fr; damien.debecker@uclouvain.be

Introduction

In a context societal awareness, catalytic recycling of CO_2 appears as very promising. TiO_2 supported Ru receives great attention as an effective catalyst in the selective hydrogenation of carbon dioxide to methane. A recently developed green method was used to prepare mono-dispersed RuO₂ nanoparticles in an aqueous colloidal suspension¹. The preparation of the controlled RuO₂ nanoparticles allows to tune their interaction with different crystalline phases of TiO_2 (rutile and anatase) and to study its influence on the catalytic conversion of CO_2 to CH₄. This work presents different behaviors of Ru on different crystal structures of TiO_2 and the synergetic effect of mixed crystal phases of TiO_2 .

Materials and Methods

Catalyst preparation. RuO₂ nanoparticles suspension was prepared by a green oxidative method¹ from RuCl₃. TiO₂ powder (Degussa P25, home-made anatase, rutile or a physical mixture thereof) was then added to the aqueous suspension to yield 2 wt. % of Ru in the final catalyst. After evaporation, the resulting powder was annealed up to 450 °C for 16 h in air and washed with water. The catalysts are characterized by TEM, HAADF-STEM, XRD, N₂ physisorption, H₂ chemisorption, and TPR.

Catalytic activity measurements. 200 mg of catalyst with particle size between 100 and 315 μ m was reduced in situ at 200 °C for 2 h under 30 ml/min of H₂ prior to the catalytic reaction. The reaction was carried out in the temperature range of 50 to 200 °C under reaction mixture of 20 ml/min (CO₂ (10 vol. %), H₂ (40 vol. %) diluted in He)

Results and Discussion

Methane production rate increased with increasing annealing temperature up to 450 °C for all TiO₂ supports (Figure 1. Left). Also, P25 support exhibited superior catalytic activity over pure anatase and rutile TiO₂. The temperature programmed reduction revealed that the 450°C-annealed catalyst was more easily reducible than 150°C-annealed catalyst at 200°C under H₂. The specific surface areas of P25-supported catalysts (~ 50 m².g⁻¹) did not change with annealing temperature, while RuO₂ supported on pure anatase and rutile TiO₂ showed almost 50% decrease in their surface areas. Sintering of the catalysts (support or/and active phase) can thus be considered as a contributor to the lower catalytic activities. This is in agreement with H₂ chemisorption where the Ru dispersion was 17.7%, 2.5%, and 14.7% for P25, anatase, and rutile supports respectively. From TEM analysis, RuO₂ nanoparticles exhibited a drastically different behavior on anatase versus rutile supports. The weak interaction between anatase TiO₂ and crystallized rutile RuO₂ phases provoked RuO₂ migration and agglomeration upon heating in air (Figure 2A). In contrast, a thin layer of crystallized RuO₂ was observed on 450 °C-annealed RuO₂/TiO₂-rutile catalyst (Figure 2C). Interestingly, the needle-shaped rutile TiO₂



Figure 1. Left: Catalytic activity at 200°C. Apparent activation energies are found out to be 14.3, 14.3 and 15.4 kcal/mol respectively for P25-, anatase-, and rutile-supported Ru catalyst. Right: Catalytic activities of Ru supported on mechanically mixed home-made anatase (80%) and rutile (20%) compared to P25, calcined at 450°C.

crystallites showed growth only in width but not length. The HAADF-STEM (Figure 2D) showed the RuO₂ layer sandwiched between (110) rutile planes with 12 nm-wide rutile crystallites, which is in correlation with the growth of rutile crystallites in width. This is an evidence for epitaxial layer formation of (110) facet of RuO₂ nanoparticles (d=3.18A) over (110) facet of TiO₂ (d=3.24A), facilitated by the close lattice parameters of rutile TiO₂ (a=4.59A, c=2.96A) and RuO₂ (a=4.49A, c=3.10A)². On P25 support, RuO₂ particles have migrated towards the TiO₂ rutile particles to form layers². TiO₂ anatase support promotes RuO₂ sintering, whereas TiO₂ rutile promotes the stable spread of RuO₂ layers. As shown in Figure 1. Right, P25 and mechanically mixed home-made anatase and rutile Phases of TiO₂ showed very similar catalytic performances. The mixed anatase- and rutile-TiO₂ as a support for Ru nanoparticles exhibited a synergetic effect on the CO₂ methanation. Anatase TiO₂ crystallites are believed to act as diluent to separate RuO₂ nanoparticles, while the co-existing rutile TiO₂ crystallites prevents the sintering of RuO₂ nanoparticles.



Figure 2. TEM images of A) RuO₂/TiO₂-anatase at 350°C, B) RuO₂/TiO₂-rutile at 150°C, C) RuO₂/TiO₂-rutile at 450°C, D) two stacked particles of RuO₂/TiO₂-rutile at 450°.

Significance

The mixture of anatase and rutile TiO_2 as a support for RuO_2 nanoparticles is highly advantageous in the design of supported catalyst owing to the possibility to balance RuO_2 - TiO_2 interactions. These results demonstrate that the morphological change of a supported catalyst have a great impact on the catalytic performance and allow us to further tune the anatase/rutile ratio in search for higher catalytic activity in various catalytic reactions.

References

- C. Sassoye, G. Muller, D. P. Debecker, A. Karelovic, S. Cassaignon, C. Pizarro, P. Ruiz, C Sanchez, Green Chem., 2011, 13, 3230-3237.
- 2. G. Xiang, X. Shi, Y. Wu, J. Zhuang, X. Wang, Sci. Rep., 2012, 2, 801