Selective CO$_2$ methanation on Ru/TiO$_2$ catalyst: unravelling the decisive role of the TiO$_2$ crystal structure

Ara Kim$^{1,*}$, Clément Sanchez, Damien P. Debecker$^{1}$, Capucine Sassoye$^{2,*}$

$^1$Institute 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 Marceau 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 RuO$_2$ nanoparticles in an aqueous colloidal suspension. The preparation of the controlled RuO$_2$ 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 CH$_4$. This work presents different behaviors of Ru on different crystal structures of TiO$_2$ and the synergistic effect of mixed crystal phases of TiO$_2$.

Materials and Methods

Catalyst preparation. RuO$_2$ nanoparticles suspension was prepared by a green oxidative method$^1$ from RuCl$_3$. TiO$_2$ 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, N$_2$ physisorption, H$_2$ chemisorption, and TPR.

Catalytic activity measurements. 200 mg of catalyst with particle size between 100 and 315 μm was reduced in situ at 200 °C for 2 h under 30 ml/min of H$_2$ 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 (CO$_2$ (10 vol. %), H$_2$ (40 vol. %) diluted in He).

Results and Discussion

Methane production rate increased with increasing annealing temperature up to 450 °C for all TiO$_2$ supports (Figure 1. Left). Also, P25 support exhibited superior catalytic activity over pure anatase and rutile TiO$_2$. The temperature programmed reduction revealed that the 450°C-annealed catalyst was more easily reducible than 150°C-annealed catalyst at 200°C under H$_2$. The specific surface areas of P25-supported catalysts (~ 50 m$^2$·g$^{-1}$) did not change with annealing temperature, while RuO$_2$ supported on pure anatase and rutile TiO$_2$ 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 H$_2$ chemisorption where the Ru dispersion was 17.7%, 2.5%, and 14.7% for P25, anatase, and rutile supports respectively. From TEM analysis, RuO$_2$ nanoparticles exhibited a drastically different behavior on anatase versus rutile supports. The weak interaction between anatase TiO$_2$ and crystallized rutile RuO$_2$ phases provoked RuO$_2$ migration and agglomeration upon heating in air (Figure 2A). In contrast, a thin layer of crystallized RuO$_2$ was observed on 450 °C-annealed RuO$_2$/TiO$_2$-rutile catalyst (Figure 2C). Interestingly, the needle-shaped rutile TiO$_2$ crystallites showed growth only in width but not length. The HAADF-STEM (Figure 2D) showed the RuO$_2$ 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 RuO$_2$ nanoparticles (d=3.18A) over (110) facet of TiO$_2$ (d=3.24A), facilitated by the close lattice parameters of rutile TiO$_2$ (a=4.49A, c=3.10A). On P25 support, RuO$_2$ particles have migrated towards the TiO$_2$ rutile particles to form layers$^2$. TiO$_2$ anatase support promotes RuO$_2$ sintering, whereas TiO$_2$ rutile promotes the stable spread of RuO$_2$ layers. As shown in Figure 1. Right, P25 and mechanically mixed home-made anatase and rutile phases of TiO$_2$ showed very similar catalytic performances. The mixed anatase- and rutile-TiO$_2$ as a support for Ru nanoparticles exhibited a synergetic effect on the CO$_2$ methanation. Anatase TiO$_2$ crystallites are believed to act as diluent to separate RuO$_2$ nanoparticles, while the co-existing rutile TiO$_2$ crystallites prevents the sintering of RuO$_2$ nanoparticles.

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