Research Paper

CO$_2$ methanation on Ru/TiO$_2$ catalysts: On the effect of mixing anatase and rutile TiO$_2$ supports

Ara Kim[a,b], Damien P. Debecker[a,*], François Devred[a], Vincent Dubois[c], Clément Sanchez[b], Capucine Sassoye[b,*]

[a] Institute of Condensed Matter and Nanosciences − Molecules, Solids and Reactivity (IMCN – MOST), Université catholique de Louvain, Place Louis Pasteur, 1, box L4. 01.09, 1348 Louvain-La-Neuve, Belgium
[b] Sorbonne Universités, UPMC Université Paris, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 4 Place Jussieu, 75252 Paris Cedex, France
[c] Institut Meurice, Laboratoire de Chimie Physique et Catalyse,Avenue Emile Gryson, 1–B-1070 Brussels, Belgium

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ABSTRACT

The high CO$_2$ methanation activity of Ru/TiO$_2$ catalysts prepared by mixing both anatase and rutile TiO$_2$ as a support is described, focusing on mild reaction temperature (50–200 °C). The specific catalyst design elucidated the impact of the support mixing. Pre-synthesized, monodispersed 2 nm-RuO$_2$ nanoparticles were used to serve as precursors for active metallic Ru responsible for the CO$_2$ hydrogenation reaction. Pure TiO$_2$ supports with different crystallinity (anatase and rutile) were either prepared in the laboratory or obtained from commercial providers, mixed, and used as supports in different ratios. The mixing was also done at different stages of the catalyst preparation, i.e. before RuO$_2$ deposition, before annealing or after annealing. Our study uncovers that the interaction between the RuO$_2$ nanoparticles and the anatase and rutile TiO$_2$ phase during the annealing step dictates the performance of the Ru/TiO$_2$ methanation catalysts. In particular, when beneficial effects of support mixing are obtained, they can be correlated with RuO$_2$ migration and stabilization over rutile TiO$_2$ through epitaxial lattice matching. Also, support mixing can help prevent the sintering of the support and the trapping of the active phase in the bulk of the sintered support. On thermally stable TiO$_2$ supports, however, it appears clearly that the sole presence of rutile TiO$_2$ support is sufficient to stabilize Ru in its most active form and to prepare a catalyst with high specific activity.

1. Introduction

In recent years, there has been increasing pressure in the society to curb CO$_2$ emissions and develop efficient CO$_2$ capture, storage and utilization technologies [1–4]. The reduction of CO$_2$ emissions is recognized as a long term task as it requires efficient use of energy and switching from fossil fuels towards less carbon intensive energy sources such as hydrogen and renewable energy [4,5]. In regard to the reduction of CO$_2$ in the atmosphere, two major strategies have been proposed: CO$_2$ capture and storage, or usage of CO$_2$ [4,6–12]. The usage of CO$_2$ is particularly promising as increasing amounts of low-cost and relatively pure CO$_2$ from current and scheduled plants for carbon capture and storage will be available at nearly zero cost [13].

Among different catalytic conversion processes of CO$_2$, the hydrogenation of CO$_2$ to methane, so-called CO$_2$ methanation, is attractive: the reaction can be carried out under atmospheric pressure, the produced CH$_4$ can be directly injected into already existing natural gas

pipelines, and it can be used as a fuel or raw material for production of other chemicals [10]. Thus, CO$_2$ methanation can serve as a tool for H$_2$ produced from renewable resources to be efficiently utilized as an energy vector since transportation of H$_2$ is limited due to its low volumetric energy density [14].

CO$_2$ methanation via heterogeneous catalysts has received considerable attention in recent years [3,10,15]. Numerous supported metals, such as Ni, Ru, Rh, Pd, Co, and Mg on various oxide supports, including TiO$_2$, SiO$_2$, Al$_2$O$_3$, CeO$_2$, MgO and ZrO$_2$, have been investigated [16–23]. The main research objective has been to obtain the best catalytic performance in terms of stability, selectivity, CO$_2$ conversion, and CH$_4$ production, especially aimed at mild reaction conditions (i.e. low reaction temperature). Ru/TiO$_2$ catalyst is widely recognized as one of the most attractive formulation [15,24–29], allowing to obtain ~100% selectivity to methane when operating under mild reaction conditions (e.g. at atmospheric pressure and ~200 °C or lower). Yet, the structure-performance relationship appears to be a key
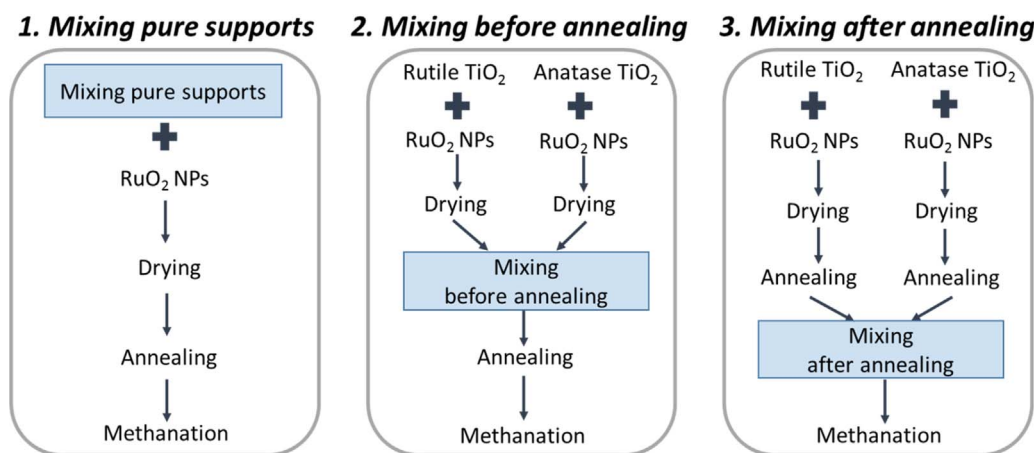
Fig. 1. Schematics of mixing anatase and rutile TiO$_2$ phases at different stages of catalyst preparation. The three routes are denoted "mixing 1", "mixing 2" and "mixing 3" in the following. Methanation step include in-situ reduction of RuO$_2$ into Ru.

for the development of high performance catalysts.

The crystal structure of TiO$_2$ support was shown to play an important role that dictates the morphology of Ru species, thereby affecting the catalytic performance in CO$_2$ methanation. In a recent contribution, we showed that Ru/TiO$_2$ catalyst supported on the commercial TiO$_2$-P25 from Degussa, which is composed of 20% rutile and 80% anatase phases, presents the highest catalytic performance compared to Ru/TiO$_2$ catalysts supported on pure anatase TiO$_2$ or rutile TiO$_2$ [24]. Our observations were in accordance with the previously reported studies in which highly dispersed and stable RuO$_2$ species were formed on rutile TiO$_2$ owing to the lattice matching with rutile TiO$_2$ support in HCl oxidation [30–32] and CO$_2$ methanation [28].

The high catalytic performance was found to be correlated to the high Ru dispersion, which itself was dictated by three phenomena [24]. First, thin layers of RuO$_2$ were formed on the rutile TiO$_2$ particles during annealing, owing to the lattice matching between rutile TiO$_2$ and rutile RuO$_2$ phases. These species generate highly dispersed Ru nanoparticles upon reduction [33]. This behavior is the opposite to the case of the anatase TiO$_2$ support onto which RuO$_2$ sinters heavily, leading to extremely low Ru dispersion in the final catalyst. Second, on the mixed support, we evidenced the migration of RuO$_2$ nanoparticles from anatase particles to rutile particles, where they maintained a good dispersion. Third, the homemade supports suffered from heavy sintering upon annealing which resulted in a significant loss of specific surface area and − more importantly − in the trapping of RuO$_2$ layers by sandwiching between rutile TiO$_2$ rods. Thus the mixed support allowed reaching higher performance because (i) it contained rutile TiO$_2$ particles which favor the dispersion of the Ru phase and (ii) it contains anatase TiO$_2$ particles from which Ru migrates, but which impede the sintering of rutile TiO$_2$ particles.

In this contribution, we present experimental data to elucidate the origin of such beneficial effect of mixing anatase and rutile. Ru/TiO$_2$ catalysts are prepared by deposition of pre-synthesized RuO$_2$ nanoparticles on mixtures of rutile and anatase TiO$_2$ with various mixing ratios while keeping other parameters constant (Ru loading and annealing condition). Rutile and anatase phases are mixed at three different stages of catalyst preparation, i.e. before RuO$_2$ deposition, before annealing, or after annealing. For those catalysts based on mixed supports at various ratio of rutile to anatase, we define "synergy" as the result of greater methane production rate as compared to the weighted average methane production rate of the pure rutile TiO$_2$ and pure anatase TiO$_2$ supported catalysts. We verify whether higher activity can be explained by the formation of more active Ru species or whether it is simply governed by dispersion. Both homemade and commercial rutile and anatase TiO$_2$ are exploited in an attempt to separate the crystalline structural effect from the effect of thermal stability (vs. sintering).

2. Experimental

2.1. Catalyst preparation

Homemade rutile and anatase TiO$_2$ supports were prepared as previously described [24]. The commercial TiO$_2$ nanopowder was obtained from Sigma-Aldrich; anatase nanopowder (99.7% trace metal basis, particle size < 25 nm) and rutile nanopowder (99.5% trace metal basis, particle size < 100 nm). A highly stable colloidal suspension of monodispersed RuO$_2$ nanoparticles [34,35] was obtained by a dropwise addition of 15%v/v H$_2$O$_2$ diluted in H$_2$O into 0.011 M RuCl$_3$·xH$_2$O (x = 3–5) dissolved in H$_2$O so that the final concentration of Ru ≈ 0.007 M. The solution was heated at 95 °C for 2 h. Once cooled to room temperature, an appropriate amount of TiO$_2$ powder was added to the colloidal suspension of RuO$_2$ nanoparticles to yield 2.2 wt.% of Ru in the final catalyst. The mixture was put in an oven at 50 °C overnight and the excess water was removed by rotary evaporation. The resulting powder was then calcined at 450 °C for 16 h in static air (this step is called "annealing" in the following).

To prepare catalysts based on the mixing of two pure supports, the mixing was done at different stages of the preparation. The schematics of catalyst preparation involving the mixing of anatase and rutile TiO$_2$ phases are shown in Fig. 1.

First, pure rutile and anatase supports were mechanically mixed in various mass ratios (rutile to anatase = 5:5, 3:7, 2:8, 1:9 for homemade TiO$_2$ supports and rutile to anatase = 5:5, 2:8 for commercial TiO$_2$ supports) followed by the deposition of RuO$_2$ NPs, drying and annealing. This procedure is referred to as "mixing 1". The catalysts are denoted as (R + A)55, (R + A)37, (R + A)28, and (R + A)19 for homemade TiO$_2$ supports and C(R + A)55 and C(R + A)28 for commercial TiO$_2$ supports respectively, where the numbers indicate the anatase-to-rutile mass ratio and "C" indicates the commercial origin of the supports.

Second, RuO$_2$ NPs were deposited and dried on rutile and anatase supports separately then mixed in various ratios right before annealing. This procedure is referred to as "mixing 2". The catalysts are noted (R + A)55-BA, (R + A)37-BA, (R + A)28-BA, and (R + A)19-BA for homemade TiO$_2$ supports and C(R + A)55-BA and C(R + A)28-BA for commercial TiO$_2$ supports, where "BA" stands for "before annealing".

Third, RuO$_2$ NPs were deposited and dried on rutile and anatase supports separately, annealed separately (i.e. the complete catalyst preparation procedure), and then mixed in various ratios. This procedure is referred to as "mixing 3". The catalysts are noted (R + A)55-AA, (R + A)37-AA, (R + A)28-AA, and (R + A)19-AA for homemade TiO$_2$ supports and C(R + A)55-AA and C(R + A)28-AA for commercial TiO$_2$ supports, where "AA" stands for "after annealing".

For comparison, pure anatase supported catalysts and pure rutile supported catalysts were prepared and denoted as A100 and R100 for