ISGC 2022

N°158 / OC
TOPIC(s) : Waste and side streams valorization / Homogenous, heterogenous and biocatalysis

Methanation of CO2 Promoted by Vacancies in Ru/TiO2 Sol-Gel Catalysts

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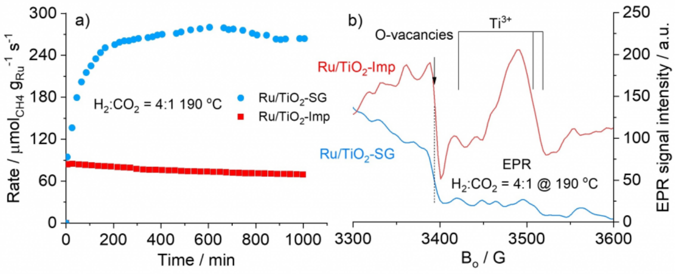
PURPOSE OF THE ABSTRACT

Hydrogenating CO2 with renewable H2 to valuable products such as CH4 is highly attractive in industry but also a big challenge, since CO2 is an extremely stable molecule which can currently be activated at sufficient rates only by expensive noble metal catalysts. This calls for the development of catalysts with maximized methanation rates but noble metal contents as low as possible.

Inspired by the primordial role of the interactions between Ru and the support for this reaction [1, 2], we developed a new Ru/TiO2-SG catalyst by an anhydrous sol-gel method that was recently designed by us for CeO2-TiO2 catalysts, in which O-vacancies played a key role for high catalytic performance [3]. This sol-gel method revealed to be very versatile to tailor heterogeneous catalysts for a variety of reactions [4]. Therefore, we used it to develop highly active CO2 methanation catalysts while limiting the Ru to 0.9 wt.%. Here, the Ru precursor was directly added to the synthesis gel. For comparison, we have also synthesized a control sample (Ru/TiO2-Imp) in which a TiO2 support prepared by the same sol-gel method was subsequently impregnated with the same amount of Ru.

From Figure 1a it is evident that the methane formation rate (normalized on the Ru mass) for catalyst Ru/TiO2-SG is ca. 3.8 times higher than that of sample Ru/TiO2-Imp. Moreover, the turnover frequencies (TOF) of our new Ru/TiO2-SG catalyst are significantly higher than those of state-of-the-art Ru/TiO2 catalysts prepared by other methods in a range between ca. 4-5 times at a temperature as low as 160 C [5, 6]. We assign the higher CO2 methanation performance of our Ru/TiO2-SG catalyst to an improved electron transfer from O-vacancies and/or Ti3+ species to interfacial Ru species under reaction conditions. These Ru species might act as H2 activation sites while O-vacancies serve as adsorption and dissociation sites for CO2. This is suggested by operando EPR spectra. These assessments unambiguously reveal pronounced signals for Ti3+ and O-vacancies occupied by single electrons in the Ru/TiO2-Imp catalyst while these are widely absent in the more active Ru/TiO2-SG catalyst (Figure 1b). This type of Ru-O-vacancy interaction, which has been recognized as determining factor to control activity and selectivity in CO2 hydrogenation reactions [1, 2], is obviously strongly enhanced by the sol-gel preparation method. Meanwhile operando DRIFTS (Figure 2) qualitatively corroborate the activity trends and suggest some differences in the adsorption layer at reaction conditions in the carbonyl and carbonates/formates region, especially at low temperatures.

FIGURES



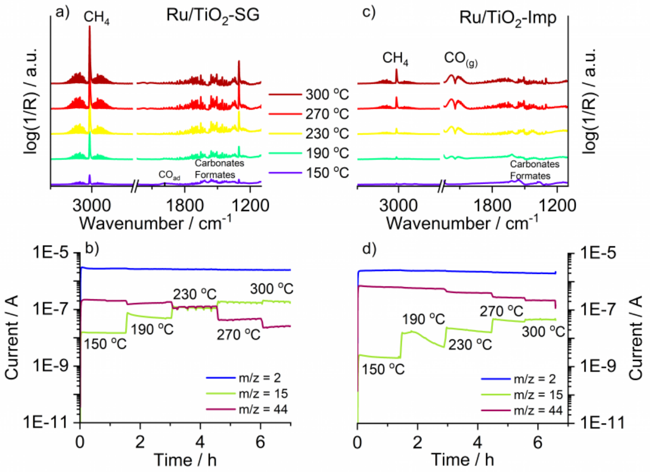


FIGURE 1

Figure 1. CO2 consumption rate (a) and EPR spectra at 190 C (b).

H2:CO2 = 4:1

FIGURE 2

Figure 2. DRIFT and mass spectra recorded during reaction at different temperatures on Ru/TiO2-SG (a, b) and on Ru/TiO2-Imp (c, d).

H2:CO2 = 4:1

KEYWORDS

CO2 | Ru | Methanation | O-vacancies

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