



Ru/Al₂O₃ catalyzed CO₂ hydrogenation: Oxygen-exchange on metal-support interfaces



Yong Yan^{a,b}, Qiaojuan Wang^a, Chunyang Jiang^a, Yao Yao^a, Di Lu^a, Jianwei Zheng^a, Yihu Dai^{a,*}, Hongming Wang^{c,*}, Yanhui Yang^{a,*}

^a Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China

^b School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore

^c Institute for Advanced Study and Department of Chemistry, Nanchang University, Nanchang 330031, China

ARTICLE INFO

Article history:

Received 13 July 2018

Revised 28 August 2018

Accepted 29 August 2018

Keywords:

CO₂

Methanation

Reverse water–gas shift

Oxygen exchange

Interface

ABSTRACT

The metal-support interfaces of metallic nanoparticles supported on oxide surfaces determine the activated dissociation of CO₂ in CO₂ hydrogenation. It also guides the catalytic pathway towards either CO₂ methanation or reverse water-gas shift (rWGS). In this work, Ru/Al₂O₃ catalysts with different Ru structural configurations were prepared by controlling the Ru weight loadings, which revealed the structure-dependence of production rates for CO and CH₄ formation with different apparent activation energies. Based on the characterization results, two catalyst models were setup: the Ru₉/Al₂O₃ model consisted of an interface of monolayer Ru sites tightly contacted with γ -Al₂O₃ support, and the Ru₃₅/Al₂O₃ model represented a relatively larger Ru nanocluster supported on γ -Al₂O₃. Theoretical calculations of these two models demonstrated that monolayer Ru sites favored the rWGS route with a relatively low energy barrier for both CO₂ activation and CO formation steps, while Ru nanoclusters preferred the methanation route energetically. Furthermore, the combination of theoretical calculations and experimental isotope-exchange measurements suggested that the interfacial O species in Ru–O–Al interfaces played a critical role in CO₂ activation via oxygen-exchanging with the O atom in the feeding CO₂ and consequently incorporation into the final hydrogenation product.

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1. Introduction

The catalytic conversion of CO₂ to useful products such as CO or carbon-neutral fuels is an essential reaction process since it involves carbon recycle with fundamental research interest and potential industrial applications as well as the environmental implications [1,2]. In consideration of the thermodynamic stability of CO₂ and the high energy barrier for splitting the C=O bond, the effective CO₂ activation deems as a critical initial step for improving the kinetics in the whole reaction of CO₂-to-chemicals transformation. Undoubtedly, it needs the rational design of promising heterogeneous catalysts based on the mechanistic understandings of CO₂ activation and reaction pathways [3–5].

The hydrogenation of CO₂ is of great significance for CO₂ utilization, for instance, it can be achieved via either reverse water-gas shift (rWGS) to yield CO or methanation to produce CH₄ [6,7].

Although the processes have been thoroughly studied from the beginning of the 20th century [8], no consensus has been reached for the activation mechanism. A bi-functional mechanism was verified on supported Pd catalysts in which H₂ dissociation on metallic Pd particles and CO₂ activated adsorption on metal oxide supports occurred synergistically to produce CH₄ via the formation of carbonates intermediates [9]. As a comparison, the Pd/SiO₂ catalyst without active oxides almost exclusively yielded CO in the CO₂ hydrogenation reaction [10,11]. This concept was further validated by the inactive performance of Pd supported on inert multi-walled carbon nanotubes [12]. In addition, another mechanism of the direct activated dissociation of CO₂ over the metal particles has been proposed for Ru and Rh catalysts [13–17], which was experimentally observed by both in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and ambient-pressure X-ray photoelectron spectroscopy (XPS) [14,15], and theoretically validated by density function theory (DFT) calculations [16]. Interestingly, both the oxygen vacancy on the support and the metallic Ru particles can serve as the activation sites for CO₂ to form CH₄ over Ru/CeO₂ but via two different reaction pathways [18].

* Corresponding authors.

E-mail addresses: ias_yhdai@njtech.edu.cn (Y. Dai), hongmingwang@ncu.edu.cn (H. Wang), yhyang@njtech.edu.cn (Y. Yang).

The interface of supported catalysts possesses dual sites of the metal-oxide heterojunction, playing pivotal roles in governing the electronic and chemical structures of the catalysts and the surface reaction process [1,19,20]. A number of structural factors in the supported metal sites, including the particle size, bimetallic alloying, crystal planes, redox ability and acidity, can finely tune the interfacial effects in the catalytic reactions [21–25]. For instance, a smaller nanocluster would be remarkably affected by the interactive multiple neighboring sites with varied geometric and electronic effects, as compared to a larger nanoparticle [26]. The acceleration of CO₂ dissociation process at the metal-support interface was observed on the supported catalysts with an optimized metal particle size [27]. On the other hand, the support-induced interfacial effects can also allow the tailoring of the electronic structure, the chemical state and the stability of the metal species for the enhancement in the catalytic performance [28,29]. In hydrogenation chemistry, both the strong metal-support interaction (SMSI) and hydrogen spillover would be subjected to the interfacial effects [30–33]. The CeO₂ supported metallic Ir nanoparticles are selective for CH₄ production, while the partially oxidized IrO_x sites that are modulated by a SMSI effect prefer selective production of CO in the hydrogenation of CO₂ [34]. Beaumont et al. have reported that a long-distance hydrogen spillover from Pt to Co sites led to the reduction of Co NPs, generating more active sites and therefore dramatically increasing CH₄ production [35]. By combining experimental characterizations and theoretical calculations, the proper metal-oxide interfaces have been demonstrated that could selectively strengthen the binding with certain surface intermediate species (e.g., ^{*}HCOO/^{*}HOCO or ^{*}CH₃O) and lead to the diverse product selectivity in the CO₂ hydrogenation reaction [36].

Herein, we choose γ -Al₂O₃-supported Ru nanoparticles as a model catalyst for studying the structure-selectivity relationship and the catalytic effects of metal-support interfaces in the CO₂ hydrogenation reaction at atmospheric pressure (1 atm). A series of characterizations such as X-ray absorption spectroscopy (XAS), H₂-O₂ titration and CO adsorption infrared spectroscopy are performed to examine the structural configurations of Ru sites in Ru/Al₂O₃ catalysts. Combining isotope-labelling kinetic experiments and theoretical calculations are also conducted to reveal the interfacial effects in the Ru-catalyzed CO₂ activation process.

2. Experimental

2.1. Catalyst preparation

Ru/Al₂O₃ catalysts with metal loadings of 1, 2 and 3 wt% were prepared on commercial γ -Al₂O₃ support (SBET of 196.5 m²/g and pore volume of 0.8 cm³/g, provided from Sigma-Aldrich, Shanghai, China) by the incipient wetness impregnation method. Typically, a certain amount of ruthenium(III) acetylacetonate (Sigma-Aldrich, Shanghai, China) was dissolved in ethanol with the pore volume of the support. The obtained solution was then added dropwise onto the support under intensive mixing. The resulting powder was dried for 12 h at 80 °C and the catalysts were then obtained via calcination at 500 °C for 2 h under 10% H₂/He with a flow rate of 100 mL/min.

2.2. Catalyst characterizations

The nitrogen adsorption-desorption isotherms at –196 °C were measured using a Quantachrome AUTO-SORB-6B static volumetric instrument. The sample was outgassed for 10 h at 200 °C before the measurement. X-ray diffraction (XRD) patterns were obtained with a Bruker AXS D8 Focus diffractometer (40 kV, 40 mA) using Cu K_α

($\lambda = 1.54 \text{ \AA}$) radiation. Scanning transmission electron microscopy (STEM) analysis was carried out on a FEI Tecnai G² F20 S-TWIN system operated at 200 kV.

The Ru K-edge extended X-ray absorption fine structure (EXAFS) spectra were measured in fluorescence mode at room temperature on the BL14W1 beam line, Shanghai Synchrotron Radiation Facility (SSRF). The storage ring was operated at 3.5 GeV and 200 mA. The synchrotron radiation was monochromatized with a Si(3 1 1) double crystal monochromator. The collected data was analyzed by Demeter software package [37] and the backscattering amplitude and phase shift were calculated using FEFF8.4 [38] during the curve fitting step. EXAFS oscillations $\chi(k)$ were extracted using spline smoothing with a Cook-Sayers criterion [39] and the filtered k^3 -weighted $\chi(k)$ was Fourier transformed into R space. The sample was pre-reduced at 500 °C in 50 mL/min of 10% H₂/He for 60 min and passivated in 50 mL/min of He for 24 h at room temperature.

H₂-O₂ titration was carried out on a Micromeritics Autochem II 2920 instrument equipped with a thermal conductivity detector (TCD) to measure the amount of surface metal sites. Typically, 100 mg of catalysts were loaded into a U-tube reactor for analysis. All samples were pretreated in 30 mL/min of H₂ flow for 60 min at 500 °C and then purged with 30 mL/min of Ar for 30 min before cooling to 30 °C in the same atmosphere. 30 mL/min of 10% O₂/Ar was passed over the samples for 30 min to allow the complete coverage of formed O species on the metal surfaces. After switching the feeding gas to pure Ar (30 mL/min), sample was heated up to 250 °C and held there until the signal was stable. Subsequently, consecutive pulses of 10% H₂/Ar (loop volume of 200 μ L) were dosed at 5 min intervals to consume all the surface oxygen. The exposed Ru surface sites was calculated with the assumed stoichiometry of H₂/Ru = 5/2 [40].

The adsorption of CO accompanied by infrared reflection absorption spectroscopy (IRAS) at 25 °C was performed on a FTIR spectrometer (Nicolet iS50) equipped with a smart collector and a MCT/A detector cooled by liquid nitrogen. Prior to each experiment, the sample was pretreated at 500 °C for 60 min in 30 mL/min of 10% H₂/He and then cooled down in 30 mL/min of He flow to 25 °C. The background spectrum was collected after 60 min in He purge (30 mL/min), followed by introducing 30 mL/min of 10% CO/He flow to start the chemisorption. After 30 min of adsorption of CO, the sample was purged in 30 mL/min of He for another 30 min and the resulted spectrum was then acquired. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

The in-situ DRIFTS of CO₂ hydrogenation reaction and surface intermediates desorption on 1% Ru/Al₂O₃ was performed on the FTIR spectrometer with MCT detector. The catalyst was pretreated with 50 mL/min of 10% H₂/Ar at 500 °C for 60 min and cooled down to 350 °C. The reaction was started when the gas flow switched to H₂/CO₂ with a ratio of 4:1. After 90 min reaction, the catalyst was purged with 30 mL/min of 10% H₂/Ar for the desorption of surface species at 350 °C for 30 min. Finally, the cell was heated up to 450 °C with 20 °C/min and kept at 450 °C for 30 min.

2.3. Kinetic measurements

For kinetic measurements, 100 mg of catalyst was loaded into a fixed-bed quartz tube micro-reactor, which was in-situ reduced in a 10% H₂/He gas flow of 100 mL/min at 500 °C for 60 min, and then kept at reaction temperature to measure the activity. The measurements were carried out at 1 atm by passing a gaseous mixture of CO₂ (5%) and H₂ (20%) in He balance at a total flow rate of 100 mL/min. The inlet and outlet flows were analyzed by an on-line gas chromatograph (Agilent 6890) equipped with a flame ionization detector (FID) and a TCD detector. The samples were taken

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