The role of vanadium in silica-supported Ru catalysts for enhanced CO_2 methanation

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Significance and Relevance

We report the first investigation into the promotional effect of vanadium on CO_2 methanation performance of Ru catalysts. This study revealed that V_2O_5 plays a beneficial role in stabilizing Ru nanoparticles and preventing their aggregation. Furthermore, hydrogen spillover from Ru during H_2 reduction and CO_2 hydrogenation promotes V_2O_5 reduction, generating oxygen vacancies and thereby facilitating electron transfer to interfacial Ru sites. This enhances CO_2 activation and CO adsorption on electronically modified Ru sites and interfacial Ru sites, significantly boosting methanation activity.

Preferred topic and 2nd choice for the topic: "Fundamental advances in understanding catalysis" and "CO_2 utilization and recycling"
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Introduction and Motivations

Converting CO_2 with green H_2 to produce CH_4 (CO_2 methanation) is a promising strategy to mitigate anthropogenic CO_2 emission while utilizing surplus green electricity (Power-to-Gas scenario).[1, 2] The promoting effects of alkali, alkali earth and lanthanide metals on Ru-based methanation catalysts have been extensively studied.[3, 4] However, little is known about the influence of transition metals – particularly vanadium – on the CO_2 methanation activity and selectivity of Ru catalysts.

Materials and Methods

The V-promoted silica materials were prepared via the aerosol-assisted sol-gel process. Tetraethyl orthosilicate, vanadium triisopropoxide, tetrapropylammonium hydroxide, and F127 surfactant were vigorously mixed to prepare the precursor solution, which was then atomized into small droplets and carried by air through the drying chamber. The dried powder was calcined at 550 °C. The loading of V was varied (x%V-SiO_2 where x = 4, 8, 12 and 16 mol%). To prepare Ru-based catalysts, the support materials were impregnated with RuO_2 nanoparticles (nominal 2 wt% Ru), which were pre-synthesized from the reaction between $RuCl_3$ and H_2O_2, and calcined at 450 °C.

Results and Discussion

An increase in V loading to 16% leads to a significant reduction in the specific surface area, from 492 m^2/g for Ru/SiO_2 to 34 m^2/g for Ru/16%V-SiO_2. Additionally, the morphology change is evident in Figure 1: Ru/SiO_2 catalyst exhibits a spherical morphology with mesopores, while Ru/16%V-SiO_2 catalyst shows an irregular shape with macropores. These changes are attributed to the formation of V_2O_5 crystallites in Ru/16%V-SiO_2, in accordance with the DRUV-vis and XRD results. Despite the decreased specific surface area, the catalytic activity of Ru/16%V-SiO_2 is markedly improved. Its methanation rate at 250 °C (168 $\mu\mathrm{mol}_{\mathrm{CO_2}}\,\mathrm{g}_{\mathrm{Ru}}^{-1}\mathrm{s}^{-1}$) is ca. 7-fold higher than that of Ru/SiO_2 (24 $\mu\mathrm{mol}_{\mathrm{CO_2}}\,\mathrm{g}_{\mathrm{Ru}}^{-1}\mathrm{s}^{-1}$), indicating that high surface area is not the determining factor for these catalysts. Instead, V_2O_5 helps stabilize Ru nanoparticles and prevent their aggregation, unlike in the case of Ru/SiO_2 catalyst, as illustrated in Figure 1. Furthermore, chemical and electronic modifications during H_2 reduction and CO_2 hydrogenation could positively influence the catalytic activity. The H_2-TPR profile of Ru/16%V-SiO_2 suggests the formation of Ru-V interaction, where hydrogen spillover from Ru facilitates further reduction of V_2O_5. Consistently, the band in the 300-500 nm region in Figure 2(a), corresponding to O^{2-}–V^{5+} charge transfer, decreases upon H_2 reduction and especially during reaction at 300 °C, indicating a decreased amount of V^{5+}. Simultaneously, a weak broad band emerges in the 500-700 nm region, attributed to the d-d transition of V^{4+} and/or V^{3+} species. The reduction of V^{5+} to V^{4+} or V^{3+} during exposure to H_2 or reactant mixture could generate oxygen vacancies, commonly regarded as a source of electron carrier. This chemical modification by oxygen-vacancy formation could lead to electronic modification of Ru sites, which affects the adsorption of key CO intermediates, as observed in the in-situ DRIFTS spectra during CO_2 methanation at 300 °C (Figure 2(b)). For Ru/16%V-SiO_2 catalyst, alongside linear CO adsorption on metallic Ru (Ru-CO at 2055-1995 cm^{-1}), V_2O_5 could promote bridge CO adsorption at the metal-support interface (Ru_{if}-CO at 1971 cm^{-1}) and linear CO adsorption on electronically modified Ru sites (2074 cm^{-1}). Promotion of CO_2 activation and CO adsorption on these active sites may facilitate electron back-donation to the adsorbed CO, weakening C-O bonds for further hydrogenation towards CH_4 formation.

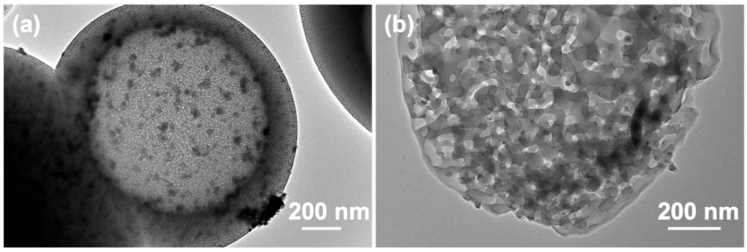

Figure 1. TEM images of (a) Ru/SiO_2 and (b) Ru/16%V-SiO_2 catalysts.

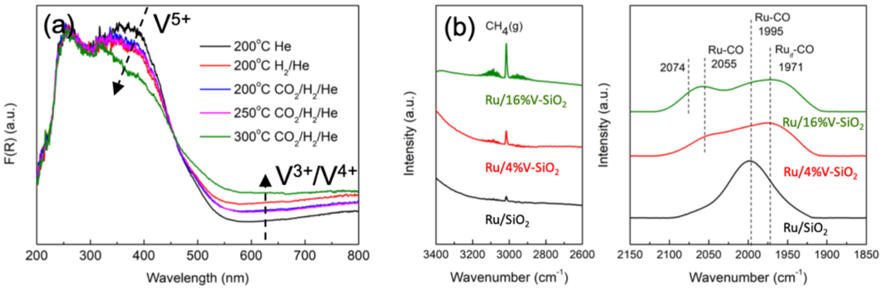

Figure 2. (a) In-situ DRUV-Vis spectra of Ru/16%V-SiO_2. (b) In-situ DRIFTS spectra during CO_2 methanation at 300 °C after 30 mins over Ru/SiO_2, Ru/4%V-SiO_2, and Ru/16%V-SiO_2 catalysts.

The CO_2 methanation activity of Ru/SiO_2 catalyst is significantly enhanced by the addition of vanadium promoter. The presence of V_2O_5 not only stabilizes Ru nanoparticles and prevents their aggregation but also provides the interaction between Ru and O-vacancies, facilitating electron transfer to interfacial Ru sites during H_2 reduction and CO_2 hydrogenation. This promotes CO_2 activation and CO adsorption on these sites, thereby improving catalytic activity in CO_2 methanation. This study enhances the understanding of the promoting effect of vanadium on CO_2 methanation. The potential of this vanadium promoter strategy could be further explored for other catalytic systems or reactions beyond CO_2 hydrogenation to CH_4.

References

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