Surface Properties and Catalytic Behavior of Ru Supported on Composite La_2O_3-SiO_2 Oxides

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Introduction

Noble metals are more active than Ni for the dry reforming of methane. As a bonus, ruthenium is much cheaper than rhodium. Furthermore, when the lantana support is used the Ru formulations are catalytically stable and do not produce carbonaceous residues [1]. Lantana helps to clean the catalyst surface by reacting with the carbon formed during the reforming of methane [1,2]. In this case, the Ru dispersion is very low, a difficulty that could be overcome when La_2O_3-SiO_2 is used as a support. The goal of this work was to study how La_2O_3 loading affects the metal dispersion and the catalyst activity and stability.

Materials and Methods

The La_2O_3-SiO_2 supports were prepared by incipient wetness impregnation of SiO_2 (Aerosil 200, calcined at 1173 K) with lanthanum nitrate. Four different lanthanum oxide loadings were employed. The wt. % of La_2O_3 is indicated between parentheses. The supports were calcined at 823 K. Metal deposition was performed by incipient wetness impregnation with $RhCl_3.3H_2O$ as precursor compound. The Ru load was 0.6 wt. %. The reaction rate measurements under differential conditions were conducted in a conventional flow system. The catalysts were heated *in situ* in an Ar flow at 823 K and then reduced in H_2 for 2 h. The reaction temperature was 823 K and the feed composition 32 vol. % CH_4, 32 vol. % CO_2, 36 vol. % Ar. The catalysts were characterized by XRD, TPR, XPS, ISS and CO chemisorption. FTIR spectroscopy with CO as a probe molecule was used to study the promoter oxide role.

Results and Discussion

The catalytic tests performed on Ru catalysts supported on La_2O_3-SiO_2 mixed oxides in a fixed-bed reactor showed that the Ru/La_2O_3(50)-SiO_2 solid exhibited the highest CH_4 TOF. The solid with the highest dispersion showed the lowest turnover frequency. All catalysts were stable for more than 100 hours on stream.

Table 1. Catalytic behavior, Ru dispersion and La/Si ratios of Ru/La_2O_3-SiO_2 catalysts.

Solids	r_{CH4} [mol h^{-1} g^{-1}]	D [%]	TOF_{CH4} [s^{-1}]	La/Si)theor	$Ru/La)_{XPS}$
Ru/La_2O_3(15)-SiO_2	0.25	40	2.92	0.18	0.175
Ru/La_2O_3(27)-SiO_2	0.21	25	3.93	0.37	0.075
Ru/La_2O_3(40)-SiO_2	0.18	72	1.17	0.67	0.049
Ru/La_2O_3(50)-SiO_2	0.40	35	5.35	1.00	0.040

The XRD broad reflections centered at 2θ = 28º and 45º are symptomatic of the presence of lanthanum disilicate that may impair the formation of oxycarbonates [2,3]. For all catalysts, the complete reduction to Ru^0 was observed through XPS. Note that the C1s peak at 289.3 eV attributed to carbonate carbon was not detected.

XPS and ISS techniques provide information on the location and distribution of the lanthanum supported phase. Typical ISS spectra are shown in Figure 1a. Both, the XPS and ISS La/Si intensity ratios increase with the La loading. For La_2O_3 wt. % higher than 40 (La/Si=0.67), the La/Si ratios present maxima (Figure 1b), suggesting the formation of multilayer or particle growth.

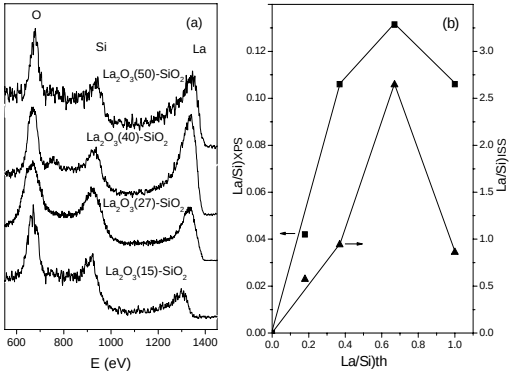

Figure 1. ISS spectra **(a)** and La/Si ratios **(b)** for the La_2O_3-SiO_2 solids.

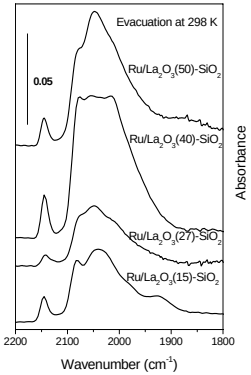

Figure 2. FTIR of Ru catalysts after CO adsorption.

The TPR reduction temperatures in the Ru/La_2O_3-SiO_2 catalysts indicate that there is an important interaction between Ru and the La-based supports. For Ru/La_2O_3(40)-SiO_2 the lowest reduction temperatures were observed in agreement with the high dispersion of this solid. The FTIR spectra of adsorbed CO of the Ru catalysts (Figure 2) after evacuation at room temperature contain a band at 2050 cm^{-1} due to linearly adsorbed CO on Ru, and the typical bands due to $Ru^{+n}(CO)_2$ carbonyls (2141, 2075, 2015 cm^{-1}). For the Ru/La_2O_3(40)-SiO_2 a significant decrease in the Ru^0-CO band is observed. This observation is in agreement with the low-methane turnover frequency and metal support interaction.

Significance

The combination of FTIR CO adsorption, TPR, ISS and XPS techniques gave valuable information about surface sites on mixed La_2O_3-SiO_2 metal catalysts. A well dispersed Ru catalyst with high CH_4 TOF was obtained, suitable for hydrogen production through the dry reforming of methane.

References

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