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Understanding the effect of Sm_2O_3 and CeO_2 promoters on the structure and activity of Rh/Al_2O_3 catalysts in methane steam reforming

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ABSTRACT

The role of Sm_2O_3 and CeO_2 promoters on the structural properties and catalytic behavior of $Rh/xSm_2O_3–yCeO_2–Al_2O_3$ catalysts during methane steam reforming (MSR) was investigated. Promoted catalysts showed higher reaction rates per surface Rh atom and improved stability compared to Rh/Al_2O_3. *In situ* X-ray absorption revealed that the structure of Rh particles in Rh/Al_2O_3 changes drastically during MSR, while it was stable in the presence of $Sm_2O_3–CeO_2$. Sintering of the active metal phase was the main cause of deactivation. STEM images showed stronger Rh agglomeration of the unpromoted catalyst with time on stream.

1. Introduction

Stricter legislation to regulate exhaust pollution and increasing interest in reducing dependence on petroleum have led to a focus on vast amounts of natural gas (methane). The conversion of methane to hydrogen and syngas has, therefore, been studied extensively. The methane steam reforming process is industrially important to obtain H_2 on a large scale [1].

The thermodynamics of methane reforming require elevated temperatures of at least 1073 K. Common problems under such conditions are carbon accumulation and metal agglomeration, thus reducing the activity of the catalyst with time on stream [2–4]. Catalysts must be resistant to carbon accumulation and stable to avoid sintering of the highly dispersed metal phase.

Through theoretical and experimental work, Jones et al. [5] confirmed that Ru and Rh are the most active pure transition metals for methane steam reforming. The activity and stability of catalysts for methane reforming are strongly influenced by the support [4,6–10]. When prepared by sol–gel precipitation, Al_2O_3 has a high surface area [11], which enables greater dispersion of the metal. The addition of structural and electronic promoters has increased the metal-support interaction and positively influenced the stability of the Al_2O_3 phases [4,8,10–12]. CeO_2 has been widely employed as a promoter for different supported metal catalysts [8,11,12]. Its superior performance is often attributed to the so-called oxygen storage capacity (OSC), which promotes the removal of carbon to maintain the accessibility of the metal sites to the reactants [13]. It has been reported that CeO_2 acts as a phase-stabilizing agent for Al_2O_3, has excellent thermal resistance, and improves the dispersion of supported metals by providing a larger metal–support interfacial region between CeO_2 and the active metal [3,6,7,14,15].

Previous studies showed that the addition of CeO_2 to noble metal/Al_2O_3-supported catalysts prevented deactivation during the reforming of methane by gasifying the deposited carbon [7,9,13]. Li et al. [16] studied the influence of CeO_2 in Al_2O_3-supported Rh catalysts for the reforming of propane and found that the addition of CeO_2 enhanced conversion by improving steam adsorption and activation. Moreover, in the presence of CeO_2, the dispersion of Rh was large and its reducibility enhanced. This improvement in performance with the addition of CeO_2 is consistent with previous reports [4,8,9,11,12].

One drawback is that CeO_2 has a low surface area and loses its OSC with a further loss of surface area at high temperature. Therefore, a better support would result from mixed CeO_2-Al_2O_3. The addition of cation modifiers with an ionic radius and electronegativity similar to CeO_2 is interesting, as they increase its OSC [17–19]. Sm_2O_3 has shown very good performance compared to other rare earth oxides in the oxidative conversion of methane [20].

Numerous publications discuss the controversial effect of the support, three of which [5,21,22] report that the oxide support

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does not influence any of the reaction steps in MSR, but that it does influence the dispersion of the metal particles. Given these reports, it is essential to elucidate the role of CeO_2 and Sm_2O_3 as dopants in catalysts to clarify the reaction mechanism and to optimize catalyst performance.

It is essential to understand how these oxides interact with each other as well as with the metal particles and how these interactions affect catalytic performance, in order to develop catalysts that transform methane. To elucidate the influence of CeO_2 and Sm_2O_3 on the structure of Rh-supported catalysts for methane reforming and to relate this to activity and stability, *in situ* X-ray absorption spectroscopy (XAS) of Sm_2O_3–CeO_2–Al_2O_3-supported Rh catalysts is a valuable tool.

The present work describes the simultaneous determination of the catalyst structure and catalyst performance, the latter of which is measured in a plug-flow reactor connected to a mass spectrometer [23]. The catalysts were studied by means of multiple techniques to understand the role played by CeO_2 and Sm_2O_3 with regard to the structure of the active phase and the cause of deactivation of active and selective catalysts, which show stable conversion during methane steam reforming.

2. Experimental

2.1. Catalyst preparation

γ-Al_2O_3 was prepared by the sol–gel method [11] by mixing aluminum tri-sec-butoxide (Aldrich 97%), 0.207 mol $Al(OC_4H_9sec)_3$, and 6.5 mol absolute ethanol (Merck) at 333 K. The gel was formed after adding water to the mixture at a water/alkoxide ratio of 14.2, while stirring and refluxing at 373 K for 1 h. Then, a solution of HNO_3 (0.109 mol/L) (Merck 67%) was added drop-wise, and the system was refluxed and stirred for 14 h at 373 K. The resulting gel was dried in air at room temperature. The solids were calcined at 773 K for 6 h.

Al_2O_3 supports, containing different amounts of Sm_2O_3 and CeO_2, were prepared by incipient wetness impregnation of the calcined γ-Al_2O_3 prepared by sol–gel synthesis with an ethanolic solution containing appropriate concentrations of $Sm(NO_3)_3{\cdot}6H_2O$ and/or $Ce(NO_3)_3{\cdot}6H_2O$. The mixture was stirred for 5 h at room temperature. The ethanol was evaporated in a roto evaporator at 328 K. The solids were dried and calcined for 12 h at 373 K and for 6 h at 1223 K. The resulting samples were xSm_2O_3–$yCeO_2$–Al_2O_3, where x and y are the theoretical concentrations of Sm_2O_3 and CeO_2, respectively, with value of 0, 6, and 12 wt.% to give $x + y = 12$ wt.%.

Rh/xSm_2O_3–$yCeO_2$–Al_2O_3 catalysts were prepared by impregnation of the respective support with a solution of $RhCl_3$ (Umicore 20%) in ethanol. The mixture was stirred for 5 h at room temperature and the solvent removed in a roto evaporator at 328 K. The samples were dried overnight at 373 K and then calcined at 873 K in air for 4 h (Scheme 1). Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES) measurements of the catalysts revealed that all the samples contain around 0.5 wt.% Rh. Catalysts supported on commercial Al_2O_3 (Condea 230 m^2/g), Sm_2O_3, and CeO_2 were also synthesized by impregnation with $RhCl_3$ as described above. Commercial Al_2O_3 was dried at 393 K for 10 h before the synthesis.

2.2. Sample characterization

Chemical analysis of the samples was carried out by Inductively Coupled Plasma–Optical emission spectrometry (ICP–OES) in a VISTA AX spectrometer (Varian, Agilent Technologies). X-ray diffraction (XRD) patterns were collected with an X'PERT PRO-MPD diffractometer with Cu Kα radiation and a Ni filter. Diffraction peaks were recorded in a 2θ range, from 5° to 80°, at intervals of 0.02 for 2 s. Nitrogen physisoption measurements were performed on a Micromeritics Tristar 3000 apparatus at 77 K. Prior to the measurements, the samples were degassed for 2 h at 473 K. The BET surface area (S_{BET}) and the average pore size diameter were calculated according to the BET and the Barret–Joyner–Halenda (BJH) methods, respectively.

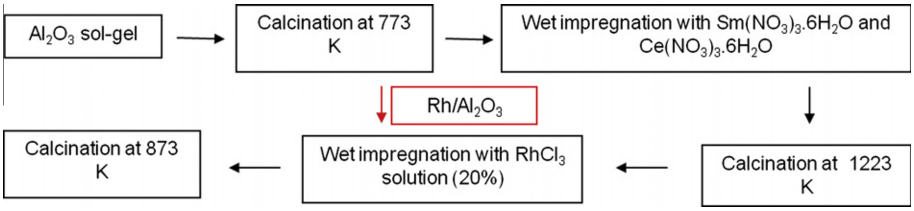
Metal particles were characterized by scanning transmission electron microscopy (STEM). STEM images were acquired with the aberration-corrected dedicated STEM microscope HD 2700 CS (Hitachi, acceleration potential of 200 kV) and obtained with a high-angle annular dark-field (HAADF) detector to produce images with atomic number (Z) contrast.

Magic-angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) was used to determine the coordination of aluminum. ^{27}Al MAS NMR experiments were performed in a Bruker Avance 700 NMR spectrometer with a 2.5 mm double-resonance probe head, operating at 182.4 MHz and a spinning speed of 15 kHz. The ^{27}Al chemical shifts were referenced to $(NH_4)Al(SO_4)_2{\cdot}12H_2O$. The pulse was 6 μm and the recycle delay was 1 s.

TGA of fresh and used Rh/xSm_2O_3–$yCeO_2$–Al_2O_3 catalysts were obtained using a Mettler Toledo TGA/SDTA851^e TGA instrument. The samples were heated from room temperature to 1273 K at 10 K min^{-1} in a flow of synthetic air (100 mL min^{-1}).

XAS measurements of the Rh catalysts were performed *in situ* during activation and the catalytic test for methane steam reforming. The experimental setup consisted of a fixed-bed capillary reactor heated by a gas blower oven. A 3 mm capillary with a wall thickness of 0.1 mm accommodated around 30 mg of the supported Rh catalysts. A mass spectrometer (GSD 300 O2, Pfeiffer Vacuum OmniStar) was attached to the end of the reactor for analysis of the product gas. Before the reaction, the catalyst was reduced at 873 K for 1.5 h under 20 mL/min of 5% H_2/He. After pretreatment, the reaction was performed with a feed containing 2.3 mL/min of 5%CH_4/He and 10 mL/min He through H_2O saturator ($H_2O/CH_4 = 3$) and a total gas flow rate of 12.3 mL/min. The temperature increased at 5 °C/min until 1033 K. It was maintained at 773 and 1033 K for 20 min to perform the XAS measurements.

In situ XAS measurements at the Rh K-edge ($E = 23{,}220$ eV) were performed at the X10DA (SuperXAS) beamline at the Swiss Light Source, Villigen, Switzerland. Extended X-ray absorption fine structure (EXAFS) scans were performed with a Si (3 1 1) double-crystal



Scheme 1. Synthesis and calcination. For the synthesis of Rh/Al_2O_3 using commercial Al_2O_3, the support was dried at 393 K for 10 h before wet impregnation with $RhCl_3$ solution (20%).