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Evaluation of $Rh/Ce_xTi_{1-x}O_2$ catalysts for synthesis of oxygenates from syngas using XPS and TPR techniques

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ABSTRACT

$Rh/Ce_xTi_{1-x}O_2$ catalysts have been investigated for the synthesis of ethanol from syngas. For this purpose various $Ce_xTi_{1-x}O_2$ ($x = 0$, 0.25, 0.5, 0.75, and 1) solid solution supports were synthesized using co-precipitation, which is an inexpensive and environmental friendly method. 2 wt% Rh has been deposited over these supports by using wet impregnation method. We have evaluated these Rh catalysts for synthesis of ethanol from syngas at atmospheric pressure and 350 psi. Among, the various catalysts, Rh supported on $Ce_{0.75}Ti_{0.25}O_2$ catalyst exhibit better selectivity toward oxygenates compared to other catalysts. Interestingly, Ti rich samples exhibit higher selectivity toward hydrocarbons while Ce rich samples exhibit higher selectivity toward oxygenated products. The catalytic results at atmospheric pressure show that titania rich catalysts exhibit higher H_2 conversion and ceria rich catalysts exhibit higher CO-conversion at 250 °C at atmospheric pressure. Temperature programmed reduction measurements suggest that Rh promotes the cerium surface reduction. X-ray photoelectron measurements show that all the catalysts exhibit peaks due to Ce^{4+} and Ce^{3+} oxidations states in the Ce 3d spectra. O1s spectra of activated Rh/TiO_2 and $Rh/Ce_{0.5}Ti_{0.5}O_2$ catalysts show two peaks after reduction in hydrogen. One peak is due to the oxygen atoms from the individual oxides and the other peak is from the compound formation between Rh and the support. X-ray photoelectron measurements of activated catalysts also show that $Rh/Ce_{0.5}Ti_{0.5}O_2$ catalyst exhibit higher Rh^{1+} ions on the surface compared to Rh/TiO_2 and exhibits better selectivity toward oxygenated products.

1. Introduction

Oxygenated carbon products like ethanol and methanol are very promising fuel alternatives and have attracted significant attention in recent years. Ethanol and Methanol are also one of the important starting feedstock for other chemicals production [1]. Methanol is produced in quantities over 50 million tons per year [2] and is present in many industrial sectors. It is used as a raw material for the synthesis of formaldehyde, one of the most important organic molecules (around 5×10^7 tons of formaldehyde produced per year) [3], for the synthesis of olefins [4,5], such as propylene and ethylene (bio polymer precursors). Ethanol is widely blended into the unleaded gasoline pool with varied percentages to significantly decreasing the dependence of our society on crude oil, at the same time reducing the harmful tailpipe emissions of CO, particulate matter, NO_x, and other pollutants. In fact, over two billion gallons of ethanol were produced in the US in 2002, mostly for use as a fuel additive [6]. Although this is small fraction of the US consumption of 134 billion gallons per year of gasoline, studies show that there is a potential to increase ethanol production to 34–75 billion gallons per year [7]. In addition to its potential application as a transportation fuel, bioethanol has been considered as a feedstock for the synthesis of variety of chemicals, fuels, and polymers. Methanol is also known as a fuel [4,8–10] either for fuel cells [11] or mixed with gasoline, or indirectly as a raw material for the synthesis of diesel, gasoline, dimethylether, hydrocarbons. Thus, the synthesis of oxygenated products like methanol, and ethanol allows getting stable and easily stored energy, as alternatives to fossil fuels. As fuels, ethanol and methanol have several ideal properties: they are nontoxic, easy to store and also transportation fuel results in lower net petroleum use and lower green house gas emissions than gasoline per mile driven. Consequently, there is a growing worldwide interest in the production of oxygenates from biomass and possibly from other readily available carbonaceous sources such as coal without CO_2 emission, and its use as a fuel for transportation, chemical feed stocks, and as an hydrogen carrier in the future.

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The catalysts for the synthesis of oxygenates from syngas can be classified into four categories: (a) Rh based catalysts [12], (b) Cu based catalysts [13], (c) modified Fisher–Tropsch catalysts [14,15], (d) modified Mo-based catalysts [16]. Among the various catalysts, Rh-based catalysts received much attention because of its high activity and its ability to adsorb reactive CO both associatively and dissociatively, allowing it to form both hydrocarbons and oxygenates [12]. Because Rh is an expensive metal, the improvement of activity and ethanol selectivity over Rh-based catalysts is necessary for achieving a commercial available process.

The mechanism of the syngas to various products over Rh based catalysts was proposed by the Arakawa et al. [16]. The main products of the reaction are hydrocarbons, oxygenates, and CO_2. According to their mechanism, first CO and H_2 adsorbs on the Rh^0 site [16]. Then, hydrogen dissociates into adsorbed hydrogen (H_{ad}). Some of the CO dissociates into carbon and atomic oxygen. Then, H_{ad} combines with C and started to form CH_x fragments. Combination of two or three CH_x fragments or addition of more H_{ad} to the CH_x fragment leads to the formation of hydrocarbons like methane, ethane, propane, etc. This reaction primarily happens on metallic Rh sites. On the other hand insertion of CO into the CH_x fragments leads to the formation of CH_2CO, CH_3CO fragments which finally are converted or rearranged into oxygenates. The insertion of CO into CH_x fragment occurs on Rh^{1+} site. Hence, the mechanism suggest that metallic Rh is mainly responsible for the CO and H_2 conversion and Rh^{1+} is responsible for the oxygenated product formation. Hence, it is important to have balance between Rh^0 and Rh^{1+} ions to have better oxygenated products yield.

The influence of various promoters on the catalytic activity of Rh has been extensively studied in recent years. Metal catalysts supported on reducible metal oxides exhibit remarkably enhanced performance in many catalytic processes, including hydrogenation [17], partial oxidation [18], or reforming reaction [19]. A strong interaction between support and metal (SMSI) exists in the CeO_2-supported metal catalysts and gives the catalysts with high activity for many catalytic reactions [20–22]. However, the main problem associated with the ceria is poor thermal stability and low lattice oxygen vacancies [23]. On the other hand, lattice oxygen of the support is very important for the SMSI interactions. Introduction of metal ions into the CeO_2 lattices improves the oxygen vacancies and catalytic performance of CeO_2-supported metal catalysts through changing the physical and chemical properties of the supports [24–26].

In the present study, we investigated the catalytic performance of $Rh/Ce_xTi_{1-x}O_2$ catalysts for the synthesis of oxygenates from syngas. Our XPS measurements show that $Ce_xTi_{1-x}O_2$ mixed oxides exhibits higher Rh^{1+} ions on the surface and exhibit better selectivity toward oxygenated products. Our catalytic measurements at atmospheric pressure show that CeO_2 and $Ce_{0.75}Ti_{0.25}O_2$ catalysts exhibits higher CO conversion and TiO_2 and $Ti_{0.75}Ce_{0.25}O_2$ catalysts exhibit higher CO conversion. Among the various catalysts $Rh/Ce_{0.75}Ti_{0.25}O_2$ catalyst exhibits best selectivity toward oxygenated products.

2. Experimental

2.1. Catalyst synthesis

2.1.1. Preparation of $Ce_xTi_{1-x}O_2$ supports

Various $Ce_xTi_{1-x}O_2$ (x = 0–1) supports were prepared by using co-precipitation method. In a typical preparation, calculated amounts of ammonium cerium nitrate and titanium chloride are dissolved separately in deionized water and the aqueous solutions mixed. Dilute aqueous ammonia was added gradually drop wise to the mixture solutions, and vigorously stirred; until precipitation was complete (pH ≈ 8.5). The obtained precipitate gels were further aged overnight, and filtered off. The obtained cakes were oven dried at 80 °C for 12 h, and finally calcined at 500 °C for 5 h. The rate of heating as well as cooling was kept at 5 °C min^{-1}.

2.1.2. Preparation of $Rh/Ce_xTi_{1-x}O_2$ catalysts

The $Rh/Ce_xTi_{1-x}O_2$ catalysts are synthesized by using wet impregnation method. In a typical synthesis, 50 mL of deionized water was added to a 100 mL beaker containing 1.0 g of support. The mixture was heated to 80 °C, under continuous stirring conditions. A predetermined quantity of rhodium nitrate precursor was then added, and the mixture was evaporated to dryness. The resulting material obtained was further dried overnight at 110 °C. Finally, the catalyst was calcined at 450 °C for 5 h.

2.2. Catalyst characterization

2.2.1. BET surface area analysis

The BET surface areas were obtained by N_2 adsorption on a Micromeritics ASAP 2010 Instrument. Prior to the analysis, samples were oven dried at 120 °C for 12 h and flushed with Argon for 2 h. The pore size distribution analyses were conducted by N_2 physisorption at liquid N_2 temperature using Micromeritics ASAP 2010 apparatus. All samples were degassed at 300 °C under vacuum before analysis.

2.2.2. X-ray diffraction measurements

Powder X-ray diffraction (XRD) patterns were recorded on a Phillips Xpert diffractometer using nickel-filtered Cu Kα (0.154056 nm) radiation source. 0–80 °C were collected using 0.02 step size and a counting time of 1 s per point. Crystalline phases were identified by comparing the observed reflections with the reference ones from ICDD files [27].

2.2.3. TPR measurements

The temperature-programmed reduction (TPR) with hydrogen, of various catalyst samples were performed by means of an automated catalyst characterization system (Micromeritics, model AutoChem II 2920), which incorporates a thermal conductivity detector (TCD). The experiments were carried out at a heating rate of 5 °C min^{-1}. The reactive gas composition was H_2 (10 vol.%) in nitrogen. The flow rate was fixed at 10 mL/min (STP). The TPR measurements were carried out following activation after cooling the sample in helium flow to 50 °C. The sample was then held at 50 °C under flowing helium to remove the remaining adsorbed oxygen until the TCD signal returned to the baseline. Subsequently, the TPR experiments were performed up to a temperature of 800 °C. The water formed during the reduction was removed by using an ice trapper. The gas stream coming from the reactor was passed through a trapper before the gas entered into the G.C. A mixture of isopropanol and liquid nitrogen was used in the trapper to remove the formed water during the TPR experiment.

2.2.4. Raman spectroscopy measurements

The Raman spectra of all the samples investigated in the present study were obtained on HORIBA Jobin Yvon HR 800 equipped with a liquid-nitrogen cooled CCD detector. The emission line at 514.5 nm from Ar^+ ion laser was focused on the sample under microscope and the analyzed spot being ~1 μm. The power of the incident beam on the sample was 3 mW. Time of acquisition was adjusted according to the intensity of the Raman scattering. The wavenumber values reported from the spectra are accurate to within 2 cm^{-1}.

2.2.5. XPS measurements

The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Pyris VG Thermo Scientific spectrometer using