

Influence of the carrier on steam reforming of acetic acid over Ru-based catalysts

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Abstract

The reaction of steam reforming of acetic acid (HAc), a model compound of pyrolysis-oil, over ruthenium catalysts supported on Al_2O_3 and $\text{MgO}/\text{Al}_2\text{O}_3$ carriers has been investigated employing transient and steady-state techniques. Main objective is the establishment of the reaction network over a wide temperature range and the elucidation of the role of MgO on intrinsic catalytic activity. It has been found that the solid-state reaction of alumina with magnesium oxide is complete, forming magnesium aluminate spinel. This carrier interacts with acetic acid and promotes mainly the ketonization reaction and, secondarily, decomposition reactions. In the presence of Ru, catalytic activity is shifted towards lower temperatures and hydrogen production occurs at high rates. Ru catalysts promote the steam-reforming reaction and retard the rate of carbon deposition onto the catalytic surface. The magnesium aluminate spinel was found to be more resistant to coke deposition compared to alumina itself. Accordingly, the $\text{Ru}/\text{MgO}/\text{Al}_2\text{O}_3$ catalyst exhibited the lowest rate of carbon deposition and was found to be significantly more active than the $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst, especially at lower temperatures. The enhanced activity of the $\text{Ru}/\text{MgO}/\text{Al}_2\text{O}_3$ catalyst seems to be associated with the fact that the magnesium aluminate spinel offers enhanced O and/or $-\text{OH}$ anion spillover from the carrier onto the metal particles and exhibits reduced surface acidity, as compared to the alumina carrier.

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1. Introduction

There is currently significant interest for the production of hydrogen for energy applications, especially hydrogen originating from renewable sources. Although the development of fuel cells meeting the criteria of high efficiency, portability and affordability faces significant technical challenges, a major hurdle remains the sourcing of hydrogen and the development of efficient, safe and affordable production processes. At present, there are many well-established processes for hydrogen production from fossil fuels, such as naphtha, natural gas and coal [1]. However, real environmental benefits are linked with the ability to produce hydrogen from renewable sources, with no net production of greenhouse gasses. A viable renewable source, gaining attention in recent years, is bio-fuels. In this respect, many reports have dealt with the steam

reforming of bio-ethanol [2–6]. Renewable lignocellulosic biomass can also be used as an alternative feedstock for hydrogen production. A technology which has been explored in recent years is the catalytic steam reforming of pyrolysis-oil. This route involves pyrolysis of biomass to generate bio-oil, and reformation of it to produce a gaseous stream rich in hydrogen. New developments in flash pyrolysis technologies make it possible to convert biomass more efficiently into bio-oil [7,8], making it an attractive alternative intermediate for hydrogen production.

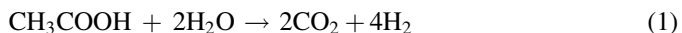
Pyrolysis-oil is a complex mixture of organic oxygenates, but its main components are more or less similar, independent of its source. Elementary analysis of bio-oil derived from different processes shows that its main components include: acids, alcohols, aldehydes, esters, ketones, sugars and phenols [9–11]. A number of studies dealing with the subject of reformation of bio-oil, using either bio-oil itself or model compounds, have been reported recently [12–20].

Acetic acid (HAc) is one of the major components of bio-oil (up to 12%) [9,10,21] and, for this reason it is often used as a

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model compound. The steam reforming of acetic acid and the water gas shift reactions occur simultaneously, and the overall stoichiometry is represented by



Steam reforming of HAc is an endothermic reaction ($\Delta H = 134.77$ kJ/mol at 298 K) which is entirely feasible from a thermodynamic point of view.

In a previous communication, it was reported that Ru-based catalysts, especially Ru supported on magnesia/alumina carrier, present high activity and high hydrogen selectivity as well as stable performance with time on stream [22]. Thus, aim of the present work was to investigate the reaction network of steam reforming of HAc over ruthenium catalysts over a wide temperature range, as well as to elucidate the role of MgO addition on Al_2O_3 on catalytic performance.

2. Experimental

2.1. Catalyst preparation and characterization

The Al_2O_3 carrier used in the preparation of catalysts is commercially available (Alfa Aesar). The $\text{MgO}/\text{Al}_2\text{O}_3$ support, as well as the $\text{Ru}/\text{Al}_2\text{O}_3$ and $\text{Ru}/\text{MgO}/\text{Al}_2\text{O}_3$ catalysts were synthesized by the wet-impregnation method, using $\text{Mg}(\text{NO}_3)_2$ and $\text{Ru}(\text{NO})(\text{NO}_3)_3$ (Alfa Aesar) as Mg and Ru precursors, respectively. The MgO content in the $\text{MgO}/\text{Al}_2\text{O}_3$ carrier was 15% by mass, while the nominal ruthenium loading in the Ru-based catalysts was 5%. Preparation of the materials has been presented in detail elsewhere [22].

Carriers and catalysts were characterized with respect to their specific surface area, exposed metallic surface area and crystallite size, employing techniques such as nitrogen physisorption (BET method), hydrogen chemisorption and X-ray diffraction (XRD) [22].

2.2. Apparatus

2.2.1. Transient experiments

Transient experiments were carried out in an apparatus consisting of a flow switching system, a heated reactor and an analysis system. The flow apparatus has been described in detail elsewhere [23]. The reactor consists of two 6.0-mm OD sections of quartz tube, which serve as inlet and outlet to and from a quartz cell of 8.0-mm OD. The total length of the reactor is 32.0 cm. The catalyst sample, approximately 100 mg, was placed in the cell and kept in place by means of quartz wool. The temperature of the catalyst was measured at the inlet of the catalyst bed by means of a K-type thermocouple placed within a quartz capillary well. An electric furnace controlled by a programmable controller provided heating to the reactor. Analysis of the gases was done by on-line mass spectrometer (VG Quadrupoles, Sensorlab 200D) equipped with a fast response inlet capillary/leak diaphragm system. The pressure in the main chamber was UHV level ($\approx 10^{-7}$ mbar). Calibration of the mass spectrometer signal was performed based on mixtures of known composition. For all experiments, gas-phase

composition was calculated from the mass spectrometer signal at *m/e* ratios of 44, 60, 58, 28, 16, 26, 27, 41, 2 for CO_2 , CH_3COOH , $(\text{CH}_3)_2\text{CO}$, CO, CH_4 , C_2H_4 , C_2H_6 , C_3H_6 and H_2 , respectively. Fragmentation of the different species was calibrated and contributions from other than the indicated ones were subtracted, as well as the background level.

2.2.2. Steady-state and kinetic experiments

Steady-state experiments were carried out using an apparatus which consists of a flow system, the reactor unit and the analysis system. The flow system consists of four mass flow controllers (MKS Instruments) for the regulation of gas flow and an HPLC pump (Marathon, Scientific Systems) for the liquid flow. The reactants are fed to a micro-reactor which is placed into an electric furnace. The analysis system comprises of two gas chromatographs (GC 14A and GC-8B, Shimadzu) and a mass spectrometer (OmniStar GSD 300, Balzers) connected in parallel through a common set of switch valves. The specific apparatus, the experimental procedure and the analytical procedure have been described in detail in a previous communication [22].

2.3. Experimental procedures

2.3.1. Adsorption of HAc and temperature-programmed desorption (TPD)

Prior to any experiment the catalyst samples were reduced *in situ* under H_2 flow ($40 \text{ cm}^3/\text{min}$) at 750°C for approximately 2 h. After purging with He for 15 min, the sample was cooled under He flow to room temperature. At this point ca. $30 \text{ cm}^3/\text{min}$ of a mixture consisting of 0.5% HAc/He was directed into the reactor chamber. Adsorption took place for 20 min at atmospheric pressure at room temperature. After purging for 15 min with He, a linear temperature ramp ($15^\circ\text{C}/\text{min}$) was initiated. The temperature ramp was terminated at 750°C and this temperature was maintained for an additional 15 min.

2.3.2. Temperature-programmed reaction (TPR)

After *in situ* reduction of the catalyst under H_2 flow ($40 \text{ cm}^3/\text{min}$) at 750°C for 1 h and purging with He for 15 min, the sample was cooled under He flow to room temperature. At this point ca. $30 \text{ cm}^3/\text{min}$ of a mixture consisting of 0.5% HAc/1.5% $\text{H}_2\text{O}/\text{He}$ was directed into the reactor chamber. These conditions were achieved by controlling the flow of three independent He lines, two of which passed through saturators with acetic acid and water. The catalyst was kept at room temperature for the first 5 min. After this period, the reactor temperature was increased rapidly (at about 1 min) to 140°C and continued increasing with a linear rate of $\beta = 15^\circ\text{C}/\text{min}$, up to 750°C .

2.3.3. Titration of deposited carbon (TPO)

The amount of carbon deposited was estimated by temperature-programmed oxidation (TPO) experiments. TPOs followed steady-state reactions for 2 h under various experimental conditions. During reaction, the catalyst was exposed to a mixture (0.5% HAc and 1.5% H_2O in He) of total flow of

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