



Hydrotalcite type materials as catalyst precursors for the Catalytic Steam Cracking of toluene



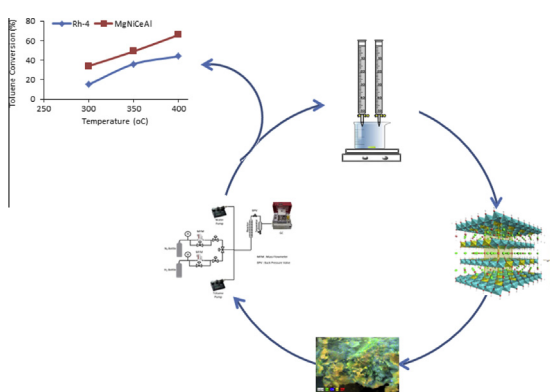
M. Josefina Pérez Zurita*, Mónica Bartolini, Thiago Righi, Gerardo Vitale, Pedro Pereira Almas

Catalysis for Bitumen Upgrading Group, Schulich School of Engineering, University of Calgary, AB, Canada

HIGHLIGHTS

- We reported on a family of novel catalysts for the Catalytic Steam Cracking of Toluene.
- In the CSC reaction the steam used for the process is a source of hydrogen.
- Highly disperse and active catalyst where obtained by the methodology employed.
- The start-up conditions have great impact in the catalytic behavior of the solids.
- The results presented have a significant economic impact.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 September 2014
 Received in revised form 27 February 2015
 Accepted 2 March 2015
 Available online 26 March 2015

Keywords:

Catalytic
 Steam
 Cracking
 Nickel
 Cerium
 Hydrotalcite

ABSTRACT

A family of nickel based mixed oxides was synthesized, characterized and tested in the CSC of Toluene. A rhodium based catalyst was also studied as a reference. The mixed oxide catalysts were prepared by the precipitation method used in the synthesis of hydrotalcite type solids and characterized by XRD, N_2 adsorption–desorption for textural properties, EDX–Field Emission Microscopy and XPS. The reference catalyst was prepared using the successive wetness impregnation method supported on $\gamma\text{-Al}_2\text{O}_3$. Successful substitution of Mg^{2+} by Ni^{2+} and that of Al^{3+} by Fe^{3+} was evidenced by XRD as the characteristic seven signals of the hydrotalcite are present in the diffractograms. All signals are slightly shifted which implies a modification on the cell parameters caused by the replacements of the cations within the structure. When Ce^{3+} was used in the synthesis a small proportion formed part of a hydrotalcite structure. However, most of it precipitated forming nano domains of CeO_2 . The hydrotalcite type nickel formulation MgNiAl and MgNiFeAl presented a poor catalytic activity as compared with the MgNiCeAl and reference catalysts. The addition of Ce seems to improve the surface properties of the catalyst and enhance the reaction performance of MgNiAl by increasing its resistance to carbon deposition. The steady state conversion of the reference rhodium catalyst at high temperature is in the same order of magnitude of that obtained with the MgNiCeAl formulation. However, MgNiCeAl shows higher conversion at lower temperatures. The presence of nanoparticles of cerium seems to be responsible for the observed results. Additionally, a high hydrogen yield was obtained. This result implies that the main reaction involved under the reaction conditions studied is steam reforming.

© 2015 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: +1 (403) 2107142.

E-mail address: mjperez@ucalgary.ca (M.J. Pérez Zurita).

1. Introduction

Catalytic Steam Cracking (CSC) is a novel approach to the upgrading of heavy oil where water is used as a source of hydrogen [1–3]. In the CSC both, total (Steam Reforming or Degradation of the Nucleus) and selective steam reforming (Steam dealkylation – SDA) take place. Total Steam Reforming is used for the production of hydrogen or syngas while in selective steam reforming only part of the hydrocarbon is gasified by water. As the selective cleavage by steam of C–C bonds requires the presence in the molecule of well differentiated C–C bonds, selective steam reforming is applied only to alkyl-aromatics. The main reaction is then a dealkylation. Hydrogen is an important chemical commodity and is produced and also consumed in a variety of processes. In the oil industry, for instance, hydrogen is used in a number of catalytic chemical processes. Hydrotreatment in refineries is one example, where hydrogen is introduced to oil fractions containing heteroatoms such as sulfur and nitrogen. Hydrogen undergoes numerous chemical reactions with the heteroatoms at certain conditions resulting in a reduction of heteroatoms content in the oil. This makes hydrogen an essential industrial constituent for heavy oil treatment.

For the SDA process, supported catalysts of group VIII metals have been studied [1]. Among them, Rh/alumina appears to be the most active and selective catalyst. However, Accurate Density Functional Theory (DFT) calculations with generalized gradient approximation and ultrasoft pseudopotentials was carried out by Pozzo et al. [4] in order to investigate the dissociation and formation of water on both Rh(111) and Ni(111) metal surfaces. The authors reported that barriers of 0.92 and 0.89 eV have to be overcome to dissociate the molecule into OH and H on the Rh(111) and Ni(111) surfaces, respectively. Further barriers of 1.03 and 0.97 eV need to be overcome to dissociate OH into O and H. The barriers for the formation of the OH molecule from isolated adsorbed O and H were found to be 1.1 and 1.3 eV, and the barriers for the formation of the water molecule from isolated adsorbed OH and H are 0.82 and 1.05 eV on the two surfaces. More importantly, these authors [4] found that the adsorption energy of the water molecule on the Rh(111) surface is roughly equal to the adsorption energy of its dissociation products, the oxygen atom and two hydrogen atoms, but on Ni(111) these dissociation products have an adsorption energy which is almost 0.5 eV lower than that of the water molecule, making the dissociation of the molecule thermodynamically advantageous [4]. This finding has important implications for the design of the catalysts to be employed to dissociate OH into O and H as the price of nickel (at the date of writing this paper) is 2400 times lower than that of Rhodium [5].

Active oxygen and hydrogen species were generated from steam when zirconia supported iron catalysts were tested in the CSC of atmospheric and vacuum residues [6]. These species reacted with the heavy oil fractions to produce lighter fractions and CO₂. Upgrading of heavy oil in the presence of steam has also been reported using natural zeolites [7] or nickel base catalysts [8].

The use of model compounds for these reactions represents a suitable approach to gain an in-depth understanding of the metal-catalysed steam cracking reactions for potential application to heavier feedstock. Toluene, alkylaromatics and condensed aromatics have been used as model molecules [1–3,9]. In recent papers, Millan et al. [2,3] reported on the use of nickel base catalysts supported on Al₂O₃ for the CSC of anthracene. They concluded that the extend of anthracene CSC depends on the nickel crystal size and that conversion values are detrimental to the selectivity towards liquid products since most of the intermediate products are further converted to the gas phase. The use of known crystalline structures such as the perovskite and hydrotalcite structures have proven to be excellent precursors for obtaining

very well dispersed metallic catalysts [10,11]. In the present work a family of nickel based mixed oxides was synthesized by the precipitation method used in the synthesis of hydrotalcite type solids and were tested in the Catalytic Steam Cracking of Toluene.

2. Experimental

2.1. Catalysts synthesis

Three hydrotalcite type solids were synthesized: Mg_{4.55}-Ni_{1.45}Al₂(OH)₁₆·CO₃·4H₂O, Mg_{4.50}Ni_{1.50}FeAl(OH)₁₆·CO₃·4H₂O and Mg_{4.30}Ni_{1.70}CeAl(OH)₁₆·CO₃·4H₂O named hereafter MgNiAl, MgNiFeAl and MgNiCeAl respectively for simplicity. The synthesis method was similar to that conventionally reported: a solution A containing appropriate quantities of Ni(NO₃)₂, Mg(NO₃)₂, Fe(NO₃)₃ and/or Al(NO₃)₃ and a solution B containing NaOH (2 M) and Na₂CO₃ (1 M) were coadded at a rate of 1 mL/min under vigorous stirring at room temperature. The final pH was 11. The resulting slurry was heated at 80 °C for 18 h and the precipitate was filtered, washed several times with distilled water until pH 7 was reached and dried at 100 °C overnight. The calcination treatment was performed on air at 450 °C overnight. The nominal nickel content in all cases was 13%. The reference rhodium catalyst Rh-4 (0.3% w/w nominal) was prepared by successive wetness impregnation. An aqueous solution of the desired concentration (1% w/w nominal each) of Ca(NO₃)₂ and KNO₃ was added slowly to a dish containing the γ-Al₂O₃ support. The coated γ-Al₂O₃ was dried at 120 °C for 3 h and calcined at 450 °C for 12 h under air flow. Finally Rhodium was impregnated with an aqueous solution of RhCl₃·3H₂O dried at 120 °C for 3 h and calcined at 450 °C for 12 h under air flow.

2.2. Catalysts characterization techniques

Powder X-ray diffraction (XRD) patterns of fresh and calcined catalysts were acquired in a Rigaku ULTIMA III X-ray diffractometer with Cu Kα radiation and 40 kV over the 2 theta range of 5–90 degrees, using a 0.02° step and a counting time of 2.0 step/s to obtain the full diffractogram for each prepared material. The XRD patterns were referenced to the powder diffraction files (International Centre for Powder Diffraction PDF 2005) using the pattern processing analysis software JADE from Materials Data Inc. The domain crystal sizes were measured using the Scherrer equation $d = (k\lambda / (B \cos \theta)) (180^\circ / \pi)$ where d is the average crystal particle diameter, k is the Scherrer constant (0.89), λ is the used wavelength (1.54056 Å for Cu) and B is the peak width at the middle height in degrees, as implemented in the commercial software JADE [12] by fitting the experimental profile to a pseudo-Voigt profile function, and then, calculating the full width at half maximum (FWHM) of the peaks. The textural properties were measured by N₂ adsorption at –196 °C in a Micromeritics TriStar 3000 automated system. Prior to the adsorption measurements, the samples were out gassed overnight at 150 °C. Nitrogen isotherms were obtained in both adsorption and desorption modes. The surface areas were determined by the BET method. The total pore volume was calculated from the amount of vapor adsorbed at a relative pressure (P/P_0) close to unity, where P and P_0 are the measured and equilibrium pressures, respectively. Pore size distribution was established from the adsorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method. A PHI VersaProbe 5000-XPS was used to record XPS spectra. The spectra were taken on samples pressed on double sided tape, using monochromatic Al source, 1486.6 eV, with a 49.3 W of power and beam diameter of 200.0 μm. A double neutralization, i.e. a low energy electron beam and low energy Ar⁺ beam, were used

Download English Version:

<https://daneshyari.com/en/article/6635403>

Download Persian Version:

<https://daneshyari.com/article/6635403>

[Daneshyari.com](https://daneshyari.com)