An experimental investigation on the effects of adding a transition metal to Ni/Al$_2$O$_3$ for catalytic hydrogenation of CO and CO$_2$ in presence of light alkanes and alkenes

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The effect of transition metals on the activity and selectivity of a Ni/Al$_2$O$_3$ catalyst for carbon oxides hydrogenation was studied. It is found that each transition metal has different and distinct promoting or inhibiting influence. Nitric oxide was used as a probe molecule to study the electronic structure of a primary and two bi-metallic catalysts. Based on a series of catalyst activity and selectivity experiments, promoted bimetallic catalysts which enhanced and inhibited the activity and selectivity of the primary Ni/Al$_2$O$_3$ catalyst were analysed by NO-FTIR experiments. The presence of multiple sites, with different electronic properties, were observed. It is concluded that the addition of transition metals to Ni/Al$_2$O$_3$ markedly changed the electronic structure of the primary catalyst. Hydrogen and carbon monoxide chemisorption experiments showed that the ratio of CO/H chemisorbed species was affected by addition of Mn and Cu to Ni/Al$_2$O$_3$. Temperature programmed desorption of H$_2$ and CO confirmed the presence of different active sites on Ni/Al$_2$O$_3$.

1. Introduction

The worldwide drive for the development of alternative energy resources is increasing due to population and industrial growth. Carbon oxides are often generated as undesirable by-products of higher hydrocarbon synthesis, especially during the partial oxidation or oxidative coupling of methane [1]. A significant concentration of carbon oxides in a hydrocarbon stream can inhibit commercialization of synthetic hydrocarbon processes [2]. Extensive research has been conducted, mainly focussing on the design of processes which increase overall efficiency and in turn reduce carbon oxides emission. Since the hydrogenation of carbon oxides was reported by Sabatier and Senderens at the beginning of the last century [3], many studies have improved the process [4]. Two of the most important and commercialized processes are Fischer-Tropsch Synthesis (FTS) to produce long chain hydrocarbons and Methanation to produce synthetic natural gas.

Nickel is a highly active transition metal for CO and CO$_2$ hydrogenation. However, nickel has not been commercialized for the FTS process due to its lighter product range being shifted towards methanation, and the formation of volatile carbonyls [5]. Although nickel has not been considered as a suitable catalyst or promoter for FTS [4], there have been research studies relevant to Ni and FTS [6]. On the other hand, numerous studies have been undertaken, with focus on methana-tion of CO and CO$_2$ over nickel catalysts to produce synthetic natural gas [7–9].

Nickel is highly active for complete conversion of carbon oxides (especially CO) and capable of producing higher hydrocarbons [2,10–12]. This is due to the high rate of CO hydrogenation and the formation of hydrogenolysis products which are observed during CO$_x$ hydrogenation reactions over nickel catalysts. The rate of formation of surface oxides, resulting in oxygenated species synthesis, is relatively low over nickel catalysts [13]. Moreover, the relatively low cost of nickel, compared to the most of metals that are active CO$_x$ hydrogenation [14], suggests nickel as a good choice for complete removal of CO$_x$ and producing light hydrocarbons. It is believed that the structural and electronic changes of the nickel catalyst have a direct influence on the performance of the catalyst in terms of both activity and selectivity during carbon oxides hydrogenation [15–18]. For instance, it has been shown that bimetallic alloys of Ni and Co have distinctly different properties when compared to single metal Ni and Co catalysts for CO hydrogenation [15]. The addition of transition metals which are believed to modify the nickel catalysts for carbon oxides hydrogenation, has been studied [15,19–21].

In this work, we present the performance of a series of bi-metallic catalysts for hydrogenation of CO and CO$_2$ in presence of light hydrocarbons. The primary focus of this study is to explore the

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influence of adding a second transition metal to Ni/Al$_2$O$_3$ on the activity; and its influence on the selectivity towards enhancing the yield of light hydrocarbons.

2. Experimental

2.1. Catalyst testing

A series of Ni-M/Al$_2$O$_3$ catalysts (Ni(NO$_3$)$_2$·6H$_2$O, Sigma-Aldrich 99.999%) were prepared using the incipient wetness method. The following transition metals were used as the second metal: Fe (Fe (NO$_3$)$_3$·9H$_2$O, Sigma-Alrich 98%), Co (Co(NO$_3$)$_2$·6H$_2$O, Sigma-Aldrich 98%), Cu (Cu(NO$_3$)$_2$·2.5H$_2$O, Sigma-Aldrich 98%), Cr (Cr(NO$_3$)$_3$·9H$_2$O, Sigma-Aldrich 99%), Mn (Mn(NO$_3$)$_2$·4H$_2$O, Sigma-Aldrich 97%), Zn (Zn (CH$_3$COO)$_2$·2H$_2$O, Chem-Supply 98%), Ru (RuCl$_3$·H$_2$O, Precious Metals Online 99%), Rh (RhCl$_3$·H$_2$O, Precious Metals Online 99%), Ag (AgNO$_3$, Ajax Chemicals 99.9%) and Cd (Cd(NO$_3$)$_2$·4H$_2$O, Aldrich 98%). Ground and calcined (at 500 °C) alumina spheres (Sasol, Alumina Spheres 1.8/ 210) are used as the support. The loading of Ni and the second transition metal in the catalysts were fixed at 6 wt% for each metal, except for the single metal Ni/Al$_2$O$_3$ in which the Ni loading is 12 wt%. For catalyst preparation, a solution of the metal precursors in distilled water was prepared for each catalyst. The solution was added dropwise to the support, with continuous mixing. The slurry was dried at 80 °C for 12 h, followed by a second 12 h drying period at 110 °C. After drying, the catalysts were calcined at 500 °C in static air. Prior to each run, the catalysts were reduced in hydrogen flow at 500 °C for 2 h. Catalyst testing experiments were performed in a fixed bed tubular reactor in a temperature range from 150 °C to 500 °C. The feed stream composition is shown in Table 1.

The feed stream contained a mixture of carbon oxides and light hydrocarbons. With this feed gas mixture, the effect of the CO$_x$ hydrogenation catalyst on the inlet hydrocarbons was determined.

2.2. Nitric oxide adsorption Fourier Transform Infra-Red Spectroscopy (NO-FTIR)

Adsorbed NO spectra were recorded at 100 °C with a Bruker Tensor27 FTIR spectrometer. Wafers with approximate weight of 15 mg were prepared by using 13 mm dies. The pressed wafers were positioned into the sample holder and placed inside the in-situ FTIR cell equipped with KBr windows. Prior to nitric oxide adsorption, the wafers were heated to 500 °C at 5 °C/min, and remained at 500 °C for 30 min under vacuum conditions. Subsequently, the catalyst samples were reduced at 500 °C by injecting hydrogen into the cell. The reduction process consisted 3 cycles of the following two steps: 10 mbar H$_2$ for 10 min, then applying vacuum to the sample for 10 min. The samples were then allowed to cool to 100 °C for NO-adsorption steps. NO-adsorption was conducted at a pressure range between 1.0×10^{-4} mbar to 10 mbar and spectra were collected with 4 cm^{-1} resolution. For difference spectra, the spectrum of the clean, activated and reduced sample at 100 °C was subtracted. To confirm the absence of any contamination, the spectrum of gas phase nitric oxide was also collected in the empty FTIR cell.

2.3. Temperature programmed desorption of H$_2$ and CO

Catalysts samples were reduced in hydrogen at 500 °C for 2hr before

every TPD analysis. The temperature programmed desorption experiments were conducted in ultra-high vacuum after the activation of the 100 mg of each sample at 500 °C for 1 h. The desorbed species were analysed by a Pfeiffer Prisma quadrupole mass spectrometer. Carbon monoxide or hydrogen adsorbed at 35 °C on fresh samples. The TPD analysis was performed with heating the saturated samples up to 500 °C following evacuation of residual gas from the system.

2.4. Hydrogen and carbon monoxide chemisorption

Volumetric chemisorption analysis involved approximately 400 mg of catalyst sample which were calcined and reduced prior to each experiment. Before the chemisorption experiments, the apparatus and sample tube were evacuated using foreground and turbo pumps. The chemisorption of hydrogen and carbon monoxide performed separately at 35 °C over a pressure range between 30 and 90 mbar. The total number of moles of gas adsorbed on the catalyst was calculated using the ideal gas law.

3. Results and discussion

3.1. Catalyst activity

The temperature controlled catalyst activity experiments were carried out over the temperature range from 150 °C to 500 °C, at atmospheric pressure. The conversion of CO and CO$_2$ started at different temperatures on different bi-metallic catalysts. The majority of CO and CO$_2$ converted to methane. The maximum conversion achieved for both CO and CO$_2$ are altered following the addition of a second transition metal to nickel. Figs. 1 and 2 show the conversion of carbon oxide as a function of reaction temperature for each catalyst.

The results disclose that the selectivity of light hydrocarbons yield is strongly dependant on the bi-metallic catalyst examined. Some transition metals (such as Mn, Fe and Rh) enhance the selectivity of C$_2$-C$_4$ production, as shown in Fig. 3. On the other hand, some transition metals (such as Cu and Ag) when added to nickel decrease the activity for CO$_x$ hydrogenation and do not improve the C$_2$-C$_4$ production yield. The changes on the catalyst activity and selectivity by adding a second metal have been attributed to a variety of reasons, most notably a change in the number of metal sites available for reaction, the formation of a suitable (enhanced catalytic activity) alloy (i.e., formation of new sites) and an enhancement in the concentration of adsorbed carbonate species on the surface of the catalyst [21].
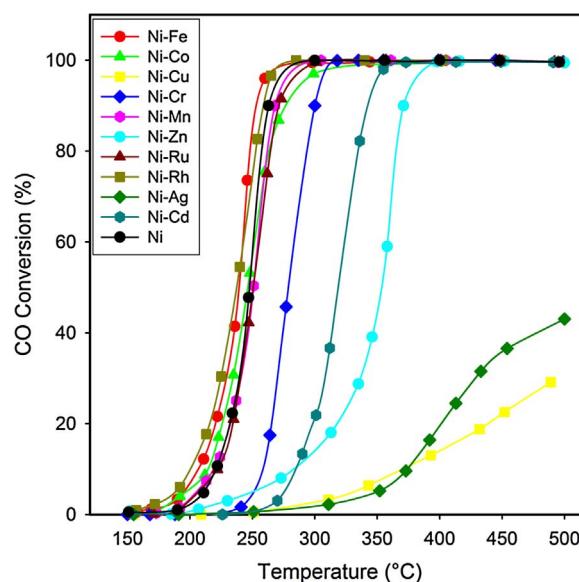
Table 1
Feed stream composition.

Partial pressure of feed species (KPa)								
H$_2$	CO	CO$_2$	CH$_4$	C$_2$H$_6$	C$_2$H$_4$	C$_3$H$_8$	C$_3$H$_6$	He
87.14	2.03	0.68	8.11	0.34	0.34	0.03	0.03	2.67

Fig. 1. Carbon monoxide conversion versus temperature over different catalysts.