CARBON OXIDES HYDROGENATION ON RhNa-Y: ADDITION OF 1-BUTENE

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At 4.0 MPa, CO₂ hydrogenation over a RhNA-Y catalyst yields only saturated and essentially linear hydrocarbons (up to C₇). In contrast, CO hydrogenation gives a more complex mixture including olefins (α and β), paraffins (linear and branched) and oxygenates. Addition of 1-butene provides a plausible interpretation of these differences.

1. Introduction

The unique ability of Rh-based catalysts to selectively hydrogenate CO into hydrocarbons, methanol or higher oxygenates is now a well established fact. Moreover, the selectivity of rhodium can be tailored to a large extent through the use of appropriate supports and promoters [1]. In order to achieve a better understanding of the factors that govern this important property, a considerable amount of work has been undertaken in recent years. Carbon monoxide hydrogenation was carried out under a variety of reaction conditions over various preparations of Rh dispersed on SiO₂, Al₂O₃, TiO₂, V₂O₅, Nb₂O₅, ZrO₂ etc., with and without other additives [2]. Surprisingly, very little has been done on Rh-zeolite catalysts [3]. On the other hand, literature reports on CO₂ hydrogenation to higher hydrocarbons are also scarce [4], even though the transformation of CO₂ into either methane or methanol is well documented [5]. The purpose of this study was therefore twofold, (a) to assess the catalytic properties of RhNa-Y in CO and in CO₂ hydrogenation under conditions favorable to high hydrocarbon formation. (b) to elucidate some of the differences between these two reactions, particularly with respect to selectivity [5].

In order to probe the catalyst surface under reaction conditions, small amounts of 1-butene were added to CO/H₂ and CO₂/H₂ feed streams, and the products originating from the added olefin were monitored. This technique has been used for some fifty years either as an investigative tool into the chemistry of CO hydrogenation or as a means of altering the product distribution of this reaction [6]. However, it appears that the olefin-probing technique has not been applied previously to CO₂ hydrogenation. In this technique, the fate of added olefin has
the potential of providing valuable information about the competition of primary product olefins for (re)adsorption and the size of "ensembles" available for further reactions. The size of such ensembles is a decisive factor for the type of secondary reactions the olefin can undergo. The choice of 1-butene offers a compromise between the simplicity of its structure and the nature of reactions it can, in principle, undergo under CO or CO\textsubscript{2} hydrogenation, i.e., hydrogenolysis, isomerization, hydrogenation and insertion into the chain growth process.

2. Experimental

RhNa-Y containing 2 w% Rh was prepared as described earlier [7] by ion exchange using a 0.002 M aqueous solution of [Rh(NH\textsubscript{3})\textsubscript{5}Cl]\textsubscript{2}. The catalytic runs were performed at 250°C in a CDS 804 Micro Pilot Plant with on-line analytical capabilities. Pretreatment of the catalyst was carried out in-situ under conditions that are known to generate a highly dispersed metallic phase with a narrow particle size distribution [8]. The catalyst, loaded in a stainless steel reactor, was first heated under flowing O\textsubscript{2} (6 L/h) up to 350°C (1°C/min), cooled under He to 250°C, then H\textsubscript{2} reduced for 3 h. The reactor was then pressurized (0.1–4.0 MPa) with an equimolar CO/H\textsubscript{2} or CO\textsubscript{2}/H\textsubscript{2} mixture flowing at 3.6 L/h.

Experiments involving 1-butene were performed at atmospheric pressure using 5% olefin in various CO/H\textsubscript{2} and CO\textsubscript{2}/H\textsubscript{2} mixtures flowing at a rate of 6 L/h.

3. Results

At low pressures (0.1–1 MPa), CO\textsubscript{2} hydrogenation yields mainly methane (~98%) and small amounts of ethane and propane. At 4.0 MPa, even though the selectivity toward methane remains very high, hydrocarbons up to C\textsubscript{7} could be easily detected and analyzed. However, beside traces of methanol, no other oxygenates were formed. Two important facts must be emphasized, (i) the distribution of C\textsubscript{2+} hydrocarbons including ethane follow a Schulz-Flory distribution (fig. 1) with a very low chain-growth probability (α = 0.34), (ii) all hydrocarbons detected were saturated and essentially linear.

In contrast, even at 0.1 MPa, CO hydrogenation gives a substantial amount of higher hydrocarbons including 1- and 2-olefins as well as linear and branched paraffins. At high pressures, a slow shift from hydrocarbons to oxygenates (largely methanol and ethanol) takes place as the reaction time increases (fig. 2). For example at 4.0 MPa and after 70 h on-stream, the following selectivities (%) were obtained: CH\textsubscript{4} = 24, C\textsubscript{2+} = 46, CH\textsubscript{3}OH = 24 and C\textsubscript{2+}–OH = 8. Similar observations have been reported by other workers [9].