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

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At 4.0 MPa, CO_2 hydrogenation over a RhNA-Y catalyst yields only saturated and essentially linear hydrocarbons (up to C_7). 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 SiO_2, Al_2O_3, TiO_2, V_2O_3, Nb_2O_5, ZrO_2 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 CO_2 hydrogenation to higher hydrocarbons are also scarce [4], even though the transformation of CO_2 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 CO_2 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/H_2 and CO_2/H_2 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 CO_2 hydrogenation. In this technique, the fate of added olefin has

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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_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 $[Rh(NH_3)_5Cl]Cl_2$. 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_2 (6 L/h) up to 350 °C (1 °C/min), cooled under He to 250 °C, then H_2 reduced for 3 h. The reactor was then pressurized (0.1–4.0 MPa) with an equimolar CO/H_2 or CO_2/H_2 mixture flowing at 3.6 L/h.

Experiments involving 1-butene were performed at atmospheric pressure using 5% olefin in various CO/H_2 and CO_2/H_2 mixtures flowing at a rate of 6 L/h.

3. Results

At low pressures (0.1–1 MPa), CO_2 hydrogenation yields mainly methane ($\sim$ 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_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_{2+} hydrocarbons *including ethane* follow a Schulz-Flory distribution (fig. 1) with a very low chain-growth probability ($\alpha = 0.34$), (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: $CH_4 = 24$, $C_{2+} = 46$, $CH_3OH = 24$ and $C_{2+}\text{-}OH = 8$. Similar observations have been reported by other workers [9].

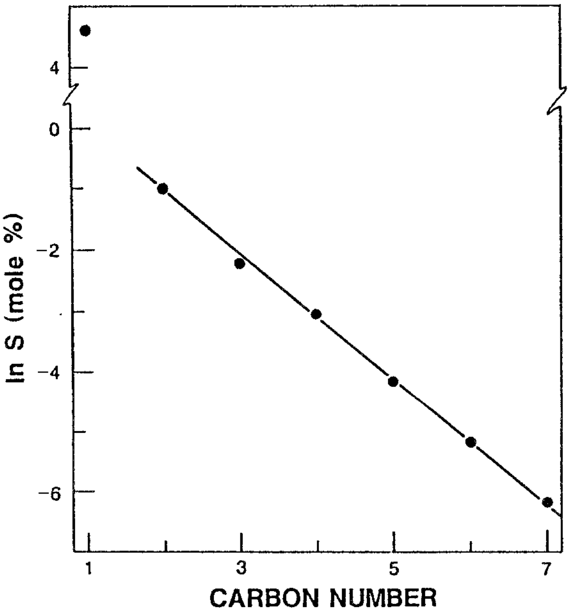

Fig. 1. Schulz-Flory plot for CO_2 hydrogenation at 4 MPa.

The main results of experiments using 1-butene are summarized in table 1. It is seen that in the absence of carbon oxides, 30% of the olefin is hydrogenated and 70% is cracked. Moreover there is a predominance of single C–C bond over multiple C–C bond splitting, a known property of Rh-based catalysts [10]. Introduction of CO_2 in an equivalent amount to 1-butene, i.e., 5%, brought about two significant changes, (i) the selectivity shifted drastically towards hydrogena-

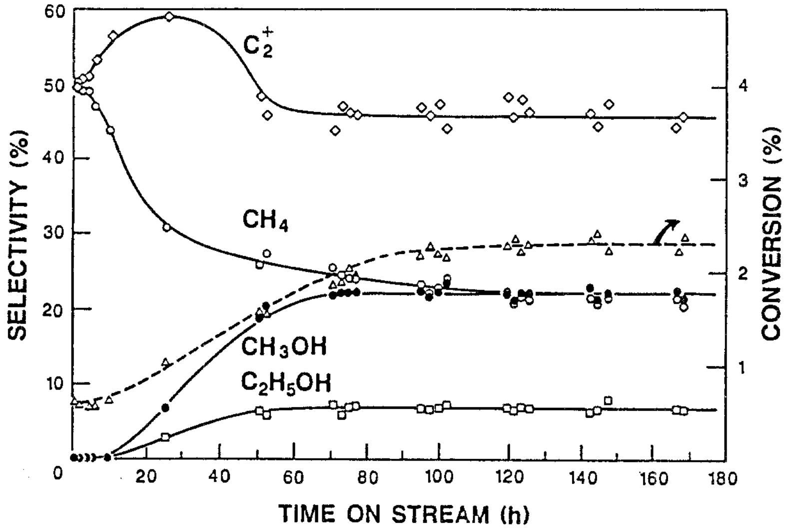

Fig. 2. CO hydrogenation at 4 MPa.

Table 1
Conversion of and product selectivity from 1-butene during CO and CO_2 hydrogenation [a]

Exp.	Feed, Composition	Conv. %	Selectivity (%)					
			Hydrogenolysis			Hydrogenation	isomerization	
			C_1	C_2	C_3	nC4	cis-$C_4^=$	Trans-$C_4^=$
1	$1\text{-}C_4^=/H_2 = 5/95$	100	25	34	11	30	0	0
2	$1\text{-}C_4^=/CO_2/H_2 = 5/5/90$	100	2	11	7	80	0	0
3	$1\text{-}C_4^=/CO_2/H_2 = 5/47.5/47.5$	99.8	0	1	0.5	95	1	1.5
4	$1\text{-}C_4^=/CO/H_2 = 5/5/90$	96	0	0	0	81	7	11
5	$1\text{-}C_4^=/CO/H_2 = 5/47.5/47.5$	66	0	0	0	0	41.5	58.5

[a] total flow = 6 L/h, catalyst = 0.3 g RhNa-Y, $t = 250\,^\circ C$, $P = 0.1$ MPa.

tion, (ii) the hydrogenolysis reactions were not inhibited to the same extent, the ratio $(C_2 + C_3)/C_1$ increasing from 1.8 to 9. This suggests that the occurrence of multiple bond breakage was more hampered by the presence of CO_2, than was the single bond cleavage. Finally, in the presence of a 1 to 1 mixture of H_2 and CO_2, the olefin was almost completely hydrogenated. Only a small amount of 1-butene (2.5%) underwent double bond shift isomerization.

In sharp contrast, the use of 5% CO in the feed inhibited completely the hydrogenolysis reactions while the hydrogenation took place to the same extent as in the case of the 5% CO_2 mixture (compare the second and fourth entries in table 1). In the presence of an equimolar mixture of CO and H_2, no hydrogenation took place while a significant fraction of the olefin (66%) underwent $\alpha \rightarrow \beta$ isomerization.

4. Discussion

As summarized in ref. [5] there have been several comparative studies of CO and CO_2 *methanation* but mostly at atmospheric pressure. Even though there is conclusive evidence that CO_2 methanation occurs through the intermediary of CO, it was found that it proceeds with a higher turnover frequency, a higher selectivity towards CH_4 and a lower activation energy than the methanation of CO. All these differences were mainly related to the high H_2/CO ratio at the catalyst surface during the methanation of CO_2.

In a very recent report, published after this work had been completed, Baird et al. [4] compared CO and CO_2 hydrogenation over Ru catalysts under typical Fischer-Tropsch conditions (21 atm, CO/H_2 and CO_2/H ratios of 1). They reported that CO_2 hydrogenation yields only linear alkanes (up to C_{17}). It was also clear from the published figures that the chain-growth probability for CO_2/H_2 reaction was lower than for CO/H_2. Again, their interpretation was based on the high concentration of hydrogen at the catalyst surface during CO_2/H_2 reaction.

Our experimental data are qualitatively very similar to those reported by Baird et al. [4]. Therefore, we concur that the difference in chain-growth probabilities for CO/H_2 and CO_2/H_2 reactions is due to the excess of hydrogen at the catalyst surface during CO_2 hydrogenation. However, it is doubtful that this excess of hydrogen is solely responsible for all hydrocarbons being saturated and linear. Indeed, if one assumes that as in CO hydrogenation, the primary products of CO_2 hydrogenation are α-olefins, the nature of secondary reactions of such olefins should involve several other parameters in addition to the availability of dissociated hydrogen [11]. First, these olefins must readsorb either on the support or on the metal. Because the support used in this study exhibits only weak acid sites, the major reactions that α-olefins can undergo on such a support are the double bond shift and cis/trans isomerizations leading to β-olefins [11]. Readsorption of either α- or β-olefins on the metallic surface depends on their ability to compete with species that occur naturally under reaction conditions, i.e. CO and C_xH_y species. Once readsorption is secured, the nature of secondary reactions on the metallic surface is believed to be dependent on at least two factors: the availability of dissociated hydrogen and the size of the "landing" site or ensemble. Experiments involving 1-butene addition were designed to shed some light on the relative importance of all these factors under both CO/H_2 and CO_2/H_2 reactions.

The first two experiments reported in table 1 clearly indicate that while the 1-butene reactions were not limited by the hydrogen supply at the catalyst surface, the addition of a small amount of CO_2 in the feed stream had a pronounced effect on the distribution of the products arising from the added alkene. This can be explained on the basis of competitive adsorption of CO_2 hydrogenation intermediates (i.e. CO and C_xH_y) and $1\text{-}C_4^=$ and the ensemble size requirements for hydrogenation vs. hydrogenolysis. It is well established that hydrogenolysis requires a larger ensemble than hydrogenation [12]. Therefore, it may be concluded that under the conditions of experiment 2 (table 1), all $1\text{-}C_4^=$ molecules had access to the metallic surface, but because of the (dynamic) blocking effect of intermediate species such as CO and C_xH_y, most of 1-butene molecules (80%) had access to only small metallic ensembles that allow their hydrogenation but not their hydrogenolysis. To explain the change in $(C_2 + C_3)/C_1$ ratio, the same reasoning may be pursued further by assuming that a multiple bond splitting requires a larger ensemble than does a single bond splitting.

Even in the presence of a much higher concentration of CO_2 (exp. 3, table 1), the olefin still hydrogenates almost quantitatively, whereas hydrogenolysis was almost completely suppressed. Only a small amount of 1-butene escaped hydrogenation and underwent $\alpha \rightarrow \beta$ isomerization which, as demonstrated earlier [11], occurs on the support.

Under the present conditions of CO_2 hydrogenation, the concentration of olefins, assumed to be primary products, at the catalyst surface is much lower than that in experiment 3. Therefore, in agreement with experimental data, these olefins undergo quantitative hydrogenation either before their first desorption or after readsorption.

The same set of experiments performed in the presence of CO instead of CO_2 led to a completely different picture. Even at 5% CO, no hydrogenolysis took place showing that the competitive adsorption is very much in favor of CO and its hydrogenation intermediates. About 17% of the olefin underwent $\alpha \to \beta$ isomerization, presumably on the support [11]. More dramatic changes took place when a higher concentration of CO was used (exp. 5, table 1). Under these conditions, the olefin was completely prevented from adsorbing and reacting on the metallic surface and only $\alpha \to \beta$ isomerization occurred.

Since either in the presence of CO/H_2 or CO_2/H_2, the added olefin competes for metallic sites against essentially the same species (i.e. adsorbed CO and C_xH_y), it may be concluded that under similar gas phase concentration of CO and CO_2, the amount of carbon-containing species adsorbed on the metal is much larger under CO/H_2 conditions than under CO_2/H_2. This may in turn be related to the excess of hydrogen at the metallic surface during CO_2/H_2 as reported in methanation studies [5].

This study demonstrates that while the hydrogen concentration at the catalyst surface is of importance in shaping the product distributions during the hydrogenation of CO and CO_2, the competitive adsorption on the metallic surface between the reactions intermediates (CO and C_xH_y) and the primary product olefins as well as the ensemble size requirements for further reactions of these olefins are also important. Additional support effects may also influence the product distribution.

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