Catalysis Letters 11 (1991) 349–356

Selective synthesis of light olefins from syngas over potassium-promoted molybdenum carbide catalysts

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Received 2 July 1991; accepted 1 November 1991

In the hydrogenation of CO at atmospheric pressure, unsupported molybdenum carbide catalyst produced mostly C_1-C_5 paraffins. Promotion of the catalyst with K_2CO_3 yielded C_2-C_5 hydrocarbons consisting of 80–100% olefins and reduced the methane selectivity. The selectivity of C_2-C_5 olefins among all hydrocarbon products was 50–70 wt% at CO conversions up to 70%.

Keywords: Molybdenum carbides; potassium promoted; CO hydrogenation; olefin selectivity

1. Introduction

The major limitation in the synthesis of hydrocarbons from H_2 and CO (syngas) is the low selectivity to the desired products [1,2]. The product distributions observed for a variety of catalyst systems and under a variety of reaction conditions conform to the Schulz–Flory polymerization equation which is inherently nonselective producing a broad range of oligomers [3]. Furthermore, product hydrocarbons contain different isomers of both paraffins and olefins. Attempts to achieve the selective production of narrow hydrocarbon fractions other than methane have seen only limited successes [2,4,5], especially in obtaining significant yields at high enough CO conversions.

Recently we have found that unsupported molybdenum carbide Mo_2C promoted with K_2CO_3 (Mo_2C/K_2CO_3) exhibits selectivities of 50–70 wt% to C_2-C_5 olefins at CO conversions up to 70%. In catalytic CO hydrogenation, this excellent light olefin selectivity has rarely been reported at such high CO conversions [4]. Light olefins are important feedstocks in the current petrochemical industry and their direct synthesis from syngas will be of a great practical significance in the future.

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2. Experimental

The unsupported Mo_2C was prepared in a manner similar to that described by Lee et al. [6]. Thus MoO_3 was heated in a flowing 20% CH_4-H_2 mixture at temperatures increasing at a rate of 30 K h^{-1} from 673 K to 973 K and at the final temperature for additional 5 h. The sample was cooled to room temperature and treated in a flow of 1% O_2 in He for 8 h to passivate the surface and then was exposed to air. Addition of K_2CO_3 was accomplished by an incipient wetness impregnation of the passivated Mo_2C with an aqueous solution of K_2CO_3 and drying at 393 K for several hours. The bulk structures of the samples were determined by X-ray diffraction (XRD), specific surface area by the N_2 BET method, and exposed metal sites by irreversible CO chemisorption at room temperature. The BET surface area and the halfwidth of XRD peak were used to estimate the particle size of Mo_2C.

The hydrogenation of CO was carried out in a flow reactor at atmospheric pressure with a mixture of $3H_2/CO$ without any diluent. The catalysts (typically 0.5 g) were treated at 670 K for 2 h in H_2 flow prior to CO chemisorption and catalytic reaction. The space velocity (SV) of the CO hydrogenation, defined as the volumetric flow rate of the syngas (STP) divided by the apparent sample volume, was maintained in the vicinity of 10000 h^{-1}, but was varied when high CO conversion data were required. Products were analyzed on an on-line gas chromatograph equipped with a Porapak-Q column and thermal conductivity/flame ionization detectors. The flame ionization detector was used to analyze hydrocarbon products heavier than C_5 which were present in minor quantity. The line between the reactor outlet and the gas chromatograph was heated at 60°C by a band heater in order to avoid potential condensation of the products in the line.

3. Results

The Mo_2C catalysts with 0–30 wt% K_2CO_3 loadings have been prepared and tested for the CO hydrogenation. The physical properties of the catalysts have been reported elsewhere [7]. Since the best olefin selectivity was observed for 12 wt% K_2CO_3-loaded Mo_2C, its properties are compared with unpromoted Mo_2C in this paper. Characterization data of these two Mo_2C catalysts are compared in table 1. The XRD showed βMo_2C with hexagonal close packed (hcp) structure as expected. Addition of K_2CO_3 reduced drastically the surface area and CO chemisorption and increased apparent particle size D_p by BET. Since the D_c by XRD remained essentially the same, the addition of K_2CO_3 appears to block exposed metal sites and pores, but not to affect the bulk structure of Mo_2C.

Table 1
Characteristics of catalysts

	Mo_2C	Mo_2C/K_2CO_3(12 wt%)
Phase by XRD	βMo_2C (hcp)	βMo_2C (hcp)
BET surface area, S_g /m^2g^{-1}	38	8
CO chemisorption [a]/μmolg^{-1}	56	0
Particle size/nm		
D_c by XRD [b]	85	88
D_p by BET [c]	177	843

[a] Irreversible chemisorption at room temperature.

[b] $D_c = \lambda / \beta \cos \theta$, λ = wavelength of CuKα X-ray radiation, β = halfwidth of diffraction peak, θ = Bragg angle.

[c] $D_p = 6/\rho S_g$, ρ = density of the solid.

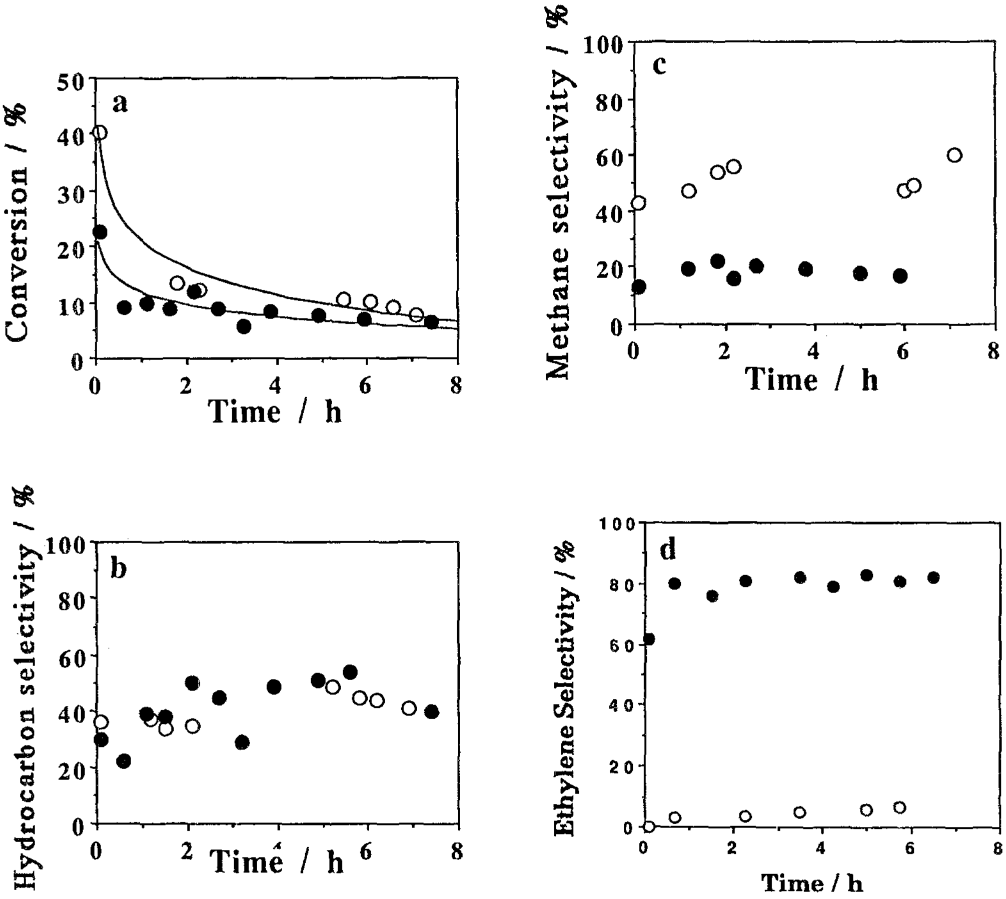

Fig. 1. The change with time on stream in CO conversion (a), the fraction of CO converted to hydrocarbons (b), CH_4 selectivity (c), and ethylene selectivity (d) observed for Mo_2C (○) and Mo_2C/K_2CO_3 (●). The CO hydrogenation was carried out at 570 K and atmospheric pressure with $3H_2$/CO and with *SV* of 10000 h^{-1}.

The hydrogenation of CO was performed at 570 K and atmospheric pressure by using $3H_2/CO$ and SV of 10000 h^{-1}. As shown in fig. 1a, both catalysts showed sharp decrease in CO conversion in the first 0.5 h of the reaction, after which steady-states were attained. For the same amount of catalyst and under the same reaction conditions, unpromoted Mo_2C showed higher CO conversion than Mo_2C/K_2CO_3, especially in the early stage of the reaction. Both catalysts produced more CO_2 than hydrocarbons as shown in fig. 1b, indicating that they were good catalysts for the water-gas shift reaction. A significant effect of K_2CO_3 promotion was seen in the methane selectivity (weight fraction of methane in hydrocarbon products, fig. 1c) and a dramatic effect in the ethylene selectivity (mole fraction of ethylene in C_2 hydrocarbons, fig. 1d).

Both catalysts produced linear paraffins and olefins up to C_7 and C_1-C_5 products accounted for more than 98% of hydrocarbons in all cases. The selectivity pattern for Mo_2C alone was similar to what has been reported

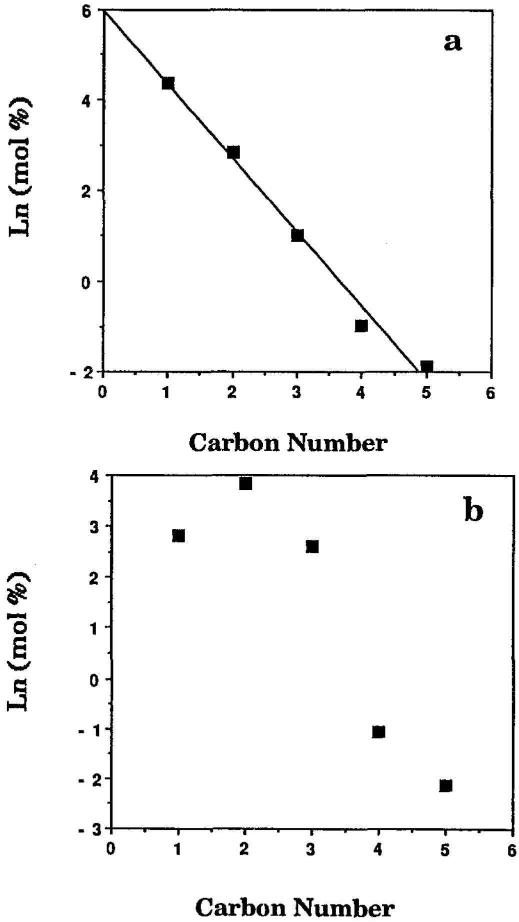

Fig. 2. Schultz-Flory plots for Mo_2C (a) and Mo_2C/K_2CO_3 (b). The CO hydrogenation was carried out at 570 K and atmospheric pressure with $3H_2/CO$ and with *SV* of 10000 h^{-1}.

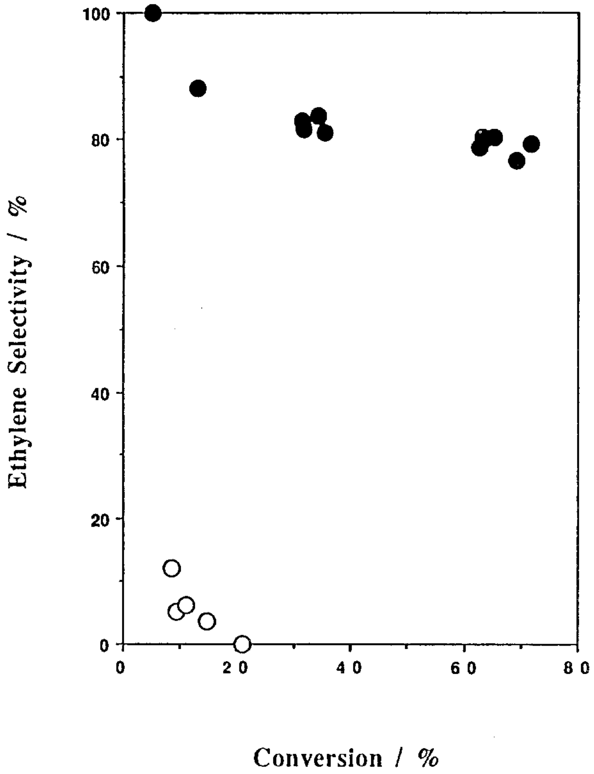

Fig. 3. Dependence of the ethylene mole % in C_2 hydrocarbon products on CO conversion: Mo_2C (o), Mo_2C/K_2CO_3 (•). The CO hydrogenation was carried out at 570 K and atmospheric pressure with $3H_2/CO$ and with *SV* of 2000–10000 h^{-1}.

elsewhere [8–10]. They produced methane and C_2-C_5 *paraffins* as predominant products. Addition of K_2CO_3 suppressed the production of methane slightly and C_2-C_5 paraffins almost completely. Instead, C_2-C_5 olefins became predominant products for Mo_2C/K_2CO_3. As shown in fig. 2a, the C_1-C_5 hydrocarbons produced from Mo_2C conformed to Schulz-Flory equation, falling on a straight line in a plot of the logarithm of the mole fraction vs. carbon number. From the slope of the plot, the probability of the chain growth of ca. 0.3 could be calculated. On the contrary, the methane fraction from Mo_2C/K_2CO_3 was significantly lower than expected by extrapolating a straight line defined by C_2-C_5 products. On the contrary, more methane and less C_2 hydrocarbons are known to be formed from group 8 metal catalysts (like Ru or Co) than expected from the distribution of heavier products. In order to find if these interesting selectivity patterns of Mo_2C/K_2CO_3 are maintained at higher CO conversions, the flow rate of H_2/CO was varied with the same amount of catalyst. The corresponding variation of *SV* ranged from 10000 to 2000 h^{-1}. As shown in fig. 3, the ethylene selectivity for Mo_2C/K_2CO_3 were near 100% at CO conversions less than 5%, and then slowly decreased to 75% at CO conversion of 70%. On

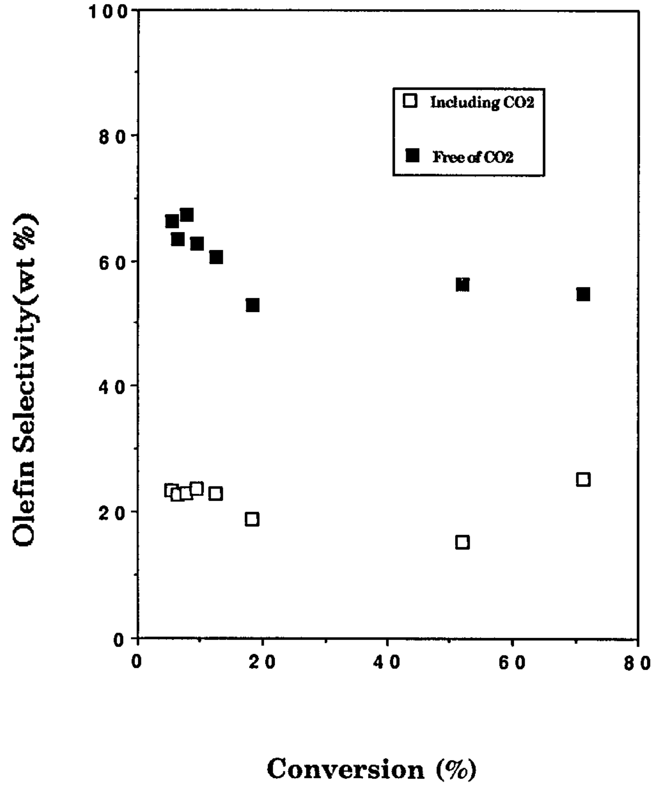

Fig. 4. Dependence of C_2-C_5 olefin wt% in products on CO conversion: The CO hydrogenation was carried out at 570 K and atmospheric pressure with $3H_2/CO$ and with *SV* of 2000–10000 h^{-1}.

the other hand, Mo_2C lost all their ethylene selectivity near the CO conversion of 20%. Similar trend was observed for propylene. The methane selectivity changed only slightly with CO conversion. Altogether, the concentration of C_2-C_5 olefins in the products was 50–70 wt% on CO_2-free basis and ca. 20 wt% including CO_2 as shown in fig. 4. The variation of the performance with time on stream was measured up to 4 h at each conversion. The change with time on stream was similar to the one shown in fig. 1. The CO conversions showed initial sharp decrease within 0.5 h and further decrease was very slow. Also, selectivity did not show any significant change after 0.5 h on stream.

4. Discussion

The product stream from Mo_2C/K_2CO_3 contained hydrocarbons, 50–70 wt% of which were C_2-C_5 olefins at CO conversions of 5–70%. This performance is similar to that for the Fe/Mn/K catalyst system which was reported to produce ca. 70% of C_2-C_4 olefins at CO conversion of 86% [4]. The system is one of the most successful examples of selectivity control in CO hydrogenation reported in the literature. Indeed, our K_2CO_3/Mo_2C and the Fe/Mn/K catalyst systems share many features in common in product distribution. Namely, both show good selectivities to C_2-C_4 olefins, suppressed methane production, and high activity to CO_2 production. The maximum C_2-C_4 species expected for the Schulz-Flory distribution is 57% [1]. Hence, these catalysts appear to operate at low degree of polymerization without giving the high yields of methane usually observed for group 8 metals. In the Fe/Mn/K system, a strong interaction between Fe and Mn was essential to observe the good performance [11]. This requirement may be a source of disagreement found for similar catalysts prepared by other investigators [5,12–14]. Our Mo_2C/K_2CO_3 must be much easier to prepare.

There have been many claims in the literature for unusual selectivity patterns and deviation from the Schulz-Flory distribution [1]. Yet only a few have been substantiated by other workers. One of the experimental problems encountered in quantifying product distribution of CO hydrogenation over heterogeneous catalysts is condensation of heavy ($> C_5$) products in the catalyst pores and in reactor downstream lines. This is not likely the case for our experiments since our products are mainly gaseous C_1-C_5 hydrocarbons. The carbon balance obtained from the CO consumption and the amount of carbon-containing products was good within ±5%.

The effect of alkali promoters in CO hydrogenation over group 8 metals is well documented [3]. They increase average chain length of hydrocarbon products and enhance the selectivity to olefins. This is indeed the direction of change that we observed when Mo_2C is promoted by K_2CO_3. However, the effects of K_2CO_3 on Mo_2C appear to be much more drastic than usually found for the group 8 metals. Furthermore, the maintenance of the selectivity at high CO conversions is of a great practical significance. It is generally accepted that the primary products of CO hydrogenation are olefins. Indeed, it has been reported that mainly olefins are produced from Mo_2C when CO conversions were less than 1% [15]. At high CO conversions, hydrogenation activity of the catalyst should be suppressed to maintain high olefin selectivity. Suppressed hydrogenation activity could also reduce the rate of methane formation which needs hydrogenation to be desorbed from the surface C_1 precursor. Hence, the selectivity pattern of Mo_2C/K_2CO_3 could be accounted for by suppressed hydrogenation activity by K_2CO_3 blocking hydrogenation sites on Mo_2C.

This work has been supported by Korean Science and Engineering Foundation through a contract 88-03-1302.

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