Synthesis of Hydrocarbons from CO and H_2 over Metal Carbide Catalysts[†]

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Summary Refractory metal carbide catalysts such as TiC, TaC, and Mo_2C catalyse the hydrogenation of carbon monoxide, producing hydrocarbons of higher molecular weight than methane.

The Fischer–Tropsch synthesis of hydrocarbons is currently an important problem in heterogeneous catalysis and a great deal of research has been conducted into this CO–H_2 reaction catalysed on metal or metal oxide surfaces. In an earlier paper,[1] it was found that the catalytic activity of powdered TaC for hydrogenation of benzene was negligible when the sample was evacuated at temperatures < 1173 K; however, it was highly activated above 1273 K. In addition,[2] similar experiments were carried out on the hydrogenation of ethylene on a series of metal monocarbides such as TaC, TiC, WC, HfC, and ZrC, to determine whether these refractory materials form a group of new sinter-resistant catalysts. It was confirmed that with TaC and TiC an enhanced activity is observed for an evacuation temperature of 1273 K. With WC, however, the activity is increased rapidly on evacuation above 873 K. We here report that powdered metal carbides such as TaC, TiC, and Mo_2C also exhibit high catalytic activities for the production of various hydrocarbons including ethylene from CO and H_2 mixtures.

The powdered metal carbides (300—350 mesh) (obtained from Materials Research Co.) were $> 99\%$ pure, and H_2 (99·999% pure) and CO (99·99%) (both obtained from Takachiho Shoji Co.) were used without further purification. All the measurements were performed in a recirculation reactor in which the products which were condensable at 78 K were continuously removed from the system during the reaction by a liquid nitrogen trap. The products were analysed by mass spectrometry and g.l.c. Before the measurements, TaC and TiC were catalytically activated by evacuation for 1 h at 1370 K. The presence of hydrogen in this pretreatment did not significantly affect the 'activation temperature,' 1370 K. With Mo_2C, the sample was reduced in hydrogen at 770 K for 2 h. In repeated reactions these carbides were evacuated for 1 h at each activation temperature, since, in subsequent reactions, the catalytic activities were found to decrease to 60—70% of those in the initial reaction and to be restored to their original levels of activity by this evacuation treatment. Mixtures of CO and H_2 gases in mole ratios from 1 : 1 to 1 : 10 with 10 Torr (1 Torr = 133·3 Pa) of CO were used as the reactant gases. The reaction temperature was kept constant at 573 K throughout the experiments.

No product was detected when hydrogen gas only was circulated on these catalysts at 573 K, which indicates that hydrogen does not react with the carbon of the carbides. The main products of CO hydrogenation on these catalysts were CH_4, H_2O, CO_2, C_2H_6, and C_2H_4; small amounts of hydrocarbons of higher molecular weight, C_3 to C_8 compounds, were also observed. CH_4 and H_2O were formed in almost equimolar amounts on Mo_2C regardless of the H_2/CO ratio; however their amounts varied on TiC and TaC surfaces. The material balance of the carbon in the reaction mixture was found to be maintained to within 10% if hydrocarbons up to C_3 were taken into consideration; apart from the hydrocarbons, the remainder of the carbon-containing products comprised mainly CO_2.

Several quantities characterizing the catalytic properties of the three metal carbides are compared in Table 1, where a mixture of CO (10 Torr) and H_2 (100 Torr) was allowed to react at 573 K; the initial rate of CO consumption decreases

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TABLE 1. Surface areas and catalytic activities of metal carbides.

	BET surface[a] area /$m^2 g^{-1}$	Initial rate of CO consumption /molecule $s^{-1} g^{-1}$	Initial rate of CH_4 formation /molecule $s^{-1} g^{-1}$	C_n-selectivity[b]
TiC	0·46	$1 \cdot 9 \times 10^{16}$	$9 \cdot 4 \times 10^{15}$	0·11
TaC	1·0	$1 \cdot 2 \times 10^{16}$	$6 \cdot 8 \times 10^{15}$	0·16
Mo_2C	0·62	$5 \cdot 6 \times 10^{15}$	$1 \cdot 8 \times 10^{15}$	0·25

[a] BET = Brunauer–Emmett–Teller. [b] (Rate of appearance of carbon in products of C_2 and above, $\Sigma_n^3 nC_n$)/(total rate of consumption of CO).

in the order TiC > TaC > Mo_2C. This trend is identical with that for the rate of CH_4 formation. However, as seen in Table 1, the selectivity for producing C_n ($n \geqslant 2$) hydrocarbons increases in this order, *i.e.*, the Mo_2C catalyst favours the production of C_2- and C_3-hydrocarbons. The change in the selectivities for production of several hydrocarbons with H_2/CO ratio is shown in Table 2, where only a small amount of the product comprises hydrocarbons larger than C_3. The selectivities depend on the H_2/CO ratio; an increase of the ratio enhances CH_4 formation and depresses the formation of olefins C_2H_4 and C_3H_6. We also observe that the selectivities of TaC and TiC are similar to each other, whereas the production of olefins, particularly ethylene, is most favourable for Mo_2C. This selectivity for olefin production is a highly desirable property.[3]

TABLE 2. %-Distributions of hydrocarbons produced.

	Mo_2C			TaC			TiC		
H_2/CO	1	3	10	1	3	10	1	3	10
$N(CH_4)/N(CO)$[a]	0·11	0·20	0·31	0·29	0·35	0·55	0·21	0·42	0·50
CH_4 (%)[b]	35·3	52·3	60·3	58·7	65·8	76·9	54·3	60·3	82·3
C_2H_4	52·2	12·2	11·6	9·3	0	0	10·4	0·9	0
C_2H_6	5·3	29·2	22·6	26·8	30·8	20·2	26·2	31·2	15·8
C_3H_6	7·2	3·6	3·3	2·8	0	0	7·0	2·6	0·5
C_3H_8	0	2·7	2·1	2·4	3·4	2·9	2·0	5·0	1·4

[a] Ratio of the initial rates of CH_4 formation to CO consumption. [b] $nC_n/\Sigma_1^3 nC_n$.

An interesting common feature of these metal carbide catalysts is that they can produce C_n ($n \geqslant 2$) hydrocarbons under conditions of high reaction temperatures and high H_2/CO ratios, which contrasts with Ru or Ni catalysts where the major hydrocarbon product is methane.[3] This difference may arise from the structural difference in the active sites between the metal carbide and the pure metal catalysts; in the metal carbides, the positive charge on the metal atom resulting from the electron transfer between the metal and carbon atoms will cause formation of multiple adsorption sites on the metal atoms required for producing hydrocarbons of higher molecular weight.

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