

ROLE OF WATER IN SYNTHESIS OF HIGHER ALCOHOLS FROM CO AND H₂ OVER MoS₂

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Experimental evidence was found in support of the direct participation of water in synthesis reactions from CO and hydrogen over MoS₂ and K/MoS₂ through its dissociation to activated OH and H. A reaction mechanism based on a common formate intermediate in alcohol and hydrocarbon synthesis and water-gas shift reaction is proposed.

Key words: Alcohol synthesis; Syn gas; MoS₂; Water-gas shift reaction.

There is interest in the synthesis of methanol and higher alcohols from carbon monoxide and hydrogen over metal sulfide catalysts at the prospect of industrial application of these catalysts in the presence of sulfur in synthesis gas. Very little is known about the reaction mechanism concerning this type of catalysts.

Based on critical analysis of literature and our own experimental data, the present work attempts at clarifying some aspects of the reaction mechanism of alcohol synthesis (AS) from CO and H₂ over MoS₂. In particular, the role of water, being direct participant in this process, is discussed.

EXPERIMENTAL

Samples of molybdenum sulfide (MoS₂) with random crystalline structure, active for mixed alcohol synthesis¹ from CO and H₂ were prepared by thermal decomposition of ammonium thiomolybdate, (NH₄)₂MoS₄, in argon atmosphere. (NH₄)₂MoS₄ was obtained through saturation of ammonium hydroxide solution of ammonium heptamolybdate (Fluka, 99.9%) with H₂S at room temperature. The precipitate was filtered, washed with methanol and ether and dried under vacuum. Further, (NH₄)₂MoS₄ was decomposed in argon flow at 450 °C. The phase composition was monitored by X-ray diffraction. K-promoted MoS₂ was prepared by impregnation of MoS₂ with aqueous solution of K₂S, followed by drying at 110 °C. The sample contained 5 wt.% K₂O.

The catalytic measurements were carried out in a stainless steel tubular down-flow fixed-bed reactor with 5 cm³ loaded catalyst under the following conditions: CO/H₂ is 1.05, synthesis gas flow rate 1 000 h⁻¹, 300 °C, and 1.6 MPa. In some experiments at atmospheric pressure the syngas contained methanol and formaldehyde of 6.7 kPa and 5.3 kPa partial pressure, respectively. In order to ensure constant catalytic activity, the samples were sulfided by H₂S at 350 °C after every 8 h of their ope-

ration. Reaction products were analyzed by gas chromatography with flame-ionization detector (FID) and hot-wire detector (HWD).

The effect of water on the product yields was studied in a glass flow reactor equipped with a device for periodic admission of water vapour. These measurements were performed under the above-mentioned conditions at atmospheric pressure.

RESULTS AND DISCUSSION

Based on the results of investigations of AS over MoS₂ reported so far, the following conclusions can be drawn. Studies of the effect of alkali promoters to MoS₂ are consistent with the conclusion that the presence of alkali is essential for the catalytic activity and selectivity towards AS. Thus it has been stated (ref.², p. 308) that "the addition of alkali metal to MoS₂ is opening a new reaction pathway" and "gives rise to the dramatic shift in selectivity from hydrocarbons to oxygenates". For example, the influence of alkali doping of MoS₂ on the product yields gives the following results with MoS₂, K/MoS₂ and Cs/MoS₂ at 295 °C, 8.2 MPa and H₂/CO 0.96 (ref.², p. 307). These are presented in Table I.

A particularly interesting fact of K-promoted catalysts is a drastic decrease in water amount, not accompanied with a respective increase in CO₂ yield. This drastic fall cannot be associated with the water–gas shift (WGS) but rather with intense synthesis of alcohols and suggests the participation of water in the process. Klier et al. (ref.², pp. 272, 273) have studied methanol synthesis over Cu/ZnO catalyst and pointed out³ that "water is a primary reactant in methanol synthesis" and that "it reacts with CO to form a formate, rather than simply forming CO₂".

Our experimental results also indicate possible water participation in AS over MoS₂. Product yields with the investigated MoS₂ and K/MoS₂ catalysts are presented in Table II. The product distributions do not substantially differ from the results reported by other authors^{1,4-7} with the same type of catalysts (ref.², p. 307). No alcohol synthesis was observed over MoS₂, except for small amounts of methanol. Water amount over K/MoS₂ was considerably less than that with MoS₂.

TABLE I
The influence of alkali doping of MoS₂ on the product yields

Catalyst	Product, g/kg _{cat} h			
	CO ₂	H ₂ O	Hydrocarbons	Alcohols
MoS ₂	235.8	135.7	192.9	2.7 ^a
K/MoS ₂	199.9	4.7	31.6	204.0
Cs/Mo ₂	259.6	2.8	56.0	319.9

^a Methanol.

TABLE II
Product yields obtained over MoS₂ and K/MoS₂ samples (mmol/g_{cat} h)

Catalyst	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	MeOH	EtOH	PrOH	BuOH	H ₂ O	CO ₂
CO + H ₂											
MoS ₂	1.30	0.02	0.95	0.40	0.17	0.10	–	–	–	3.04	5.08
K/MoS ₂	1.15	0.04	0.80	0.20	0.05	1.02	0.25	0.64	–	1.40	5.24
CO + H ₂ O											
MoS ₂	0.45	0.10	0.20	0.05	–	0.33	–	–	–	^a	71.7
K/MoS ₂	0.52	0.45	0.25	0.12	0.10	0.62	0.37	0.25	–	^a	98.4
CO + H ₂ + CH ₂ O											
MoS ₂	10.30	0.10	2.50	0.20	–	0.32	0.04	–	–	^a	23.3
K/MoS ₂	8.92	0.64	2.20	0.45	0.12	2.74	0.34	0.10	0.02	^a	27.3
CO + H ₂ + MeOH											
MoS ₂	0.77	–	1.95	0.75	0.01	^a	4.05	1.00	0.02	2.94	27.3
K/MoS ₂	0.54	–	0.45	0.53	–	^a	4.12	1.33	0.14	2.68	21.5

^a Not measured.

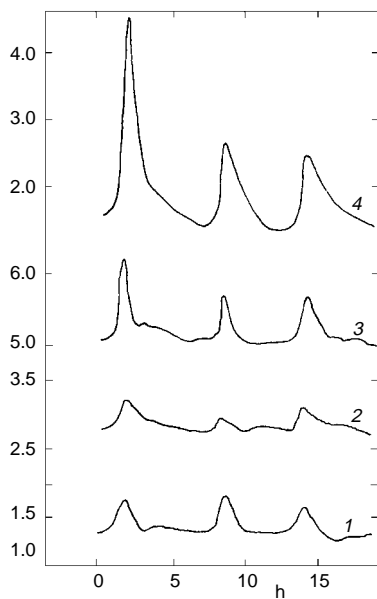


FIG. 1
Products and water content (in mmol/g_{cat} h) in the reaction mixture over a K/MoS₂ sample: 1 alcohols, 2 C_nH_{2n+2} + C_nH_{2n}, 3 CO₂, and 4 H₂O

Figure 1 shows the dependence of alcohol, hydrocarbon and CO₂ yields (in mmol/g_{cat} h) over K/MoS₂ on the amount of water in the reaction mixture. Introduction of additional quantities of water into the reaction system leads to a pronounced stimulation of the three main directions of the process: AS, hydrocarbon synthesis (HS), and WGS. The effect of water on the hydrocarbon and CO₂ yields is considerably weaker with the MoS₂ sample (Fig. 2).

The direct participation of water in the conversion of synthesis gas (CO + H₂) over K/MoS₂ and MoS₂ can reasonably be related to the participation of reactive hydroxyl groups formed upon interaction of water with the catalyst. The promoting effect of water in methanol synthesis over copper–zinc catalysts is associated with the formation of formate intermediate on interaction of CO with surface hydroxyl groups⁸. The formation of formate species has also been suggested for the WGS mechanism on low-temperature copper catalysts⁹. Together with alcohol and hydrocarbon synthesis, the WGS reaction also takes place to a large extent on K/MoS₂ and MoS₂.

Probable reaction mechanisms of the processes occurring over K/MoS₂ and MoS₂ catalysts in syngas conversion are shown in Scheme 1. A principal intermediate, specific of the three main reaction paths, is the surface formate formed upon interaction of CO with OH group. A linear formate species is assumed to be more reactive than the commonly discussed bridged species^{9–11}. Upon admission of formaldehyde to the CO + H₂ mixture (Table II), the alcohols and CO₂ yields are increased, in favour of formate participation in AS and WGS reaction. Scheme 1 suggests that formaldehyde forms a surface methoxy species which is hydrated to a formate intermediate.

A considerable part of the scheme is relevant to water activation to form an activated hydroxyl group. Studies of sulfide ion oxidation to elementary sulfur in aqueous solution over NiPS₃ (ref.¹²) and MoS₂ (ref.¹³) catalysts gave evidence for water activation, dissociated to OH and H, by means of intercalation into the catalyst. Water activation takes place under the polarizing influence of the fields of alkali ion and chalcogenide

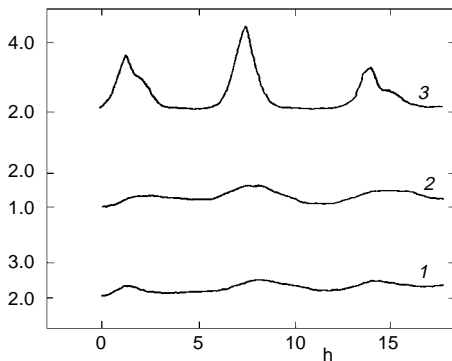


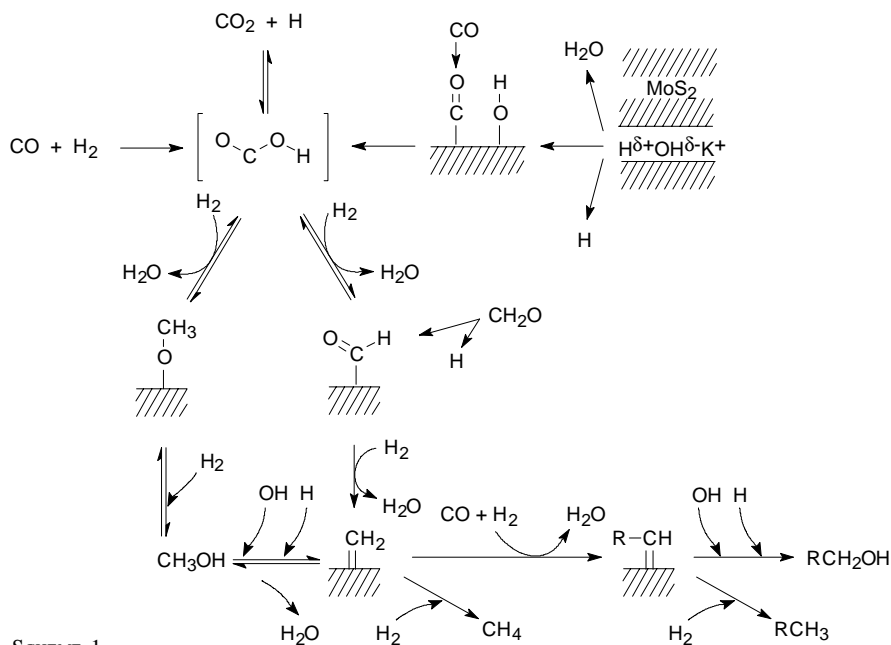
FIG. 2
Products and water content (in mmol/g_{cat} h) in the reaction mixture over a MoS₂ sample: 1 C_nH_{2n+2} + C_nH_{2n}, 2 CO₂, and 3 H₂O

layer in the van der Waals gap at “edge sites” (Scheme 1). Such a type of polarized water intercalated into transition metal sulfides has been experimentally found¹⁴ by NMR.

Further, the proposed scheme follows some of the steps of the scheme reported by Hinderman et al.⁸. It is presumed that the paths of chain growth are the same for hydrocarbons and alcohols over the alkali-doped MoS₂ catalyst¹⁵. It is also assumed that most likely carbenes take part in HS by chain growth^{8,16,17}. The most important suggestion in Scheme 1 is the possibility of alcohol synthesis through direct interaction between the carbene species and a hydroxyl group. It should be noted that atomic hydrogen, formed as a result of water decomposition, has to take an active part in the hydrogenation processes. This may also contribute to the stimulating effect of water, for example in HS.

The suggested scheme explains the stimulating influence of water on the three reaction paths of AS, HS and WGS, all being related to a common formate intermediate formed through the participation of an activated hydroxyl group originated from water decomposition. The occurrence of alcohol and hydrocarbon synthesis due to the interaction between CO and H₂O (Table II) can be interpreted in favour of the proposed reaction mechanism (Scheme 1). The formation of a common formate intermediate with the participation of water can be assumed to be more realistic than its formation from CO and hydrogen, the latter being the product of WGS reaction.

This scheme also accounts for the stimulating effect of the alkali promoter on alcohol synthesis. Under the influence of alkali cations intercalated into MoS₂, water dissoci-



SCHEME 1

ation can proceed, and the activated hydroxyl group formed can take part in synthesis reactions.

The possibility of direct formation of formate species from CO and hydrogen⁸ is important for reasonable evaluation of the results obtained with MoS₂ and K/MoS₂. Water dissociative decomposition on a nonpromoted sample proceeds to a lower extent, the hydrocarbon synthesis being accomplished via a formate species formed upon interaction between carbon monoxide and hydrogen followed by processes of hydrogenation of carboxylate species⁸. The presence of small amounts of methanol on MoS₂ can also be explained. In particular, the introduction of methanol to the reaction mixture leads to enhanced amounts of hydrocarbons and higher alcohols (Table II). This can be explained by assuming methanol dehydration to a surface carbene species which further takes part in hydrocarbon and alcohol synthesis.

This scheme provides a possibility of CO₂ participation in synthesis reactions¹⁸ through the formation of formate intermediate via a reverse WGS.

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