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Factors affecting the carbonylation of methanol over sulfided CoMo / C catalysts at atmospheric pressure

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Methanol carbonylation has been carried out over carbon supported sulfided CoMo catalysts without addition of CH_3I, as promoter, to the feed. A temperature around 250°C, and methanol concentrations higher than 5 mol% were found to be optimum for ester production. Sulfided Mo / C catalysts were inactive for methanol carbonylation, methane being the major product. While sulfided Co / C catalysts were as effective for ester production as CoMo / C catalysts, methanol conversion was higher in the latter. The selectivity to methyl acetate was found to be strongly dependent on the nature of the carbon support.

Keywords: sulfided CoMo catalysts; supported catalysts; active carbon support; vapor phase carbonylation; methanol carbonylation

1. Introduction

The synthesis of methyl acetate from methanol is an attractive process for the chemical industry. Although homogeneous carbonylation of methanol is a highly selective process [1,2], it is affected by the disadvantages associated with a highly corrosive reaction medium due to the use of methyl iodide as promoter, and difficult product separation. In order to overcome these problems, there have been many attempts to "heterogenize" various catalytically active transition metal complexes; for example, supported rhodium complexes [3,4], and nickel and iridium based catalysts [5,6], some of them supported on activated carbons [4–6].

In addition, methanol and higher alcohol synthesis from $CO + H_2$ [7] is known to be catalyzed by alkali doped Mo and CoMo sulfides. However, these sulfides have not received much attention for methanol carbonylation.

Within the above scope, it is the aim of the present work to study in some detail the reaction of methanol with CO over sulfided CoMo catalysts supported on activated carbon without requiring CH_3I in the feed as promoter.

2. Experimental

Three different commercial active carbons were employed as supports. These solids were characterized by their BET surface areas, ash content and surface pH values. The surface pH is defined as the final pH after mixing the carbon with water ($pH = 7$) under reflux condition and inert atmosphere (N_2) for 1 h.

Catalysts were prepared by incipient wetness impregnation of the supports. Molybdenum was first impregnated using ammonium heptamolybdate solution, followed by drying at 120°C overnight. The solid was then impregnated with cobalt nitrate and drying again at 120°C overnight. The composition of the catalyst ($y/x = CoO/MoO_3$ weight ratio) was adjusted by using appropriate concentrations in the impregnating solution. Prior to the catalytic tests, the dried catalysts were sulfided in situ with H_2S, at 400°C for 2 h.

Methanol carbonylation was carried out in a fixed bed type reactor with a continuous flow system at atmospheric pressure. The gaseous reactants (carbon monoxide or a mixture CO/H_2) were saturated with methanol by bubbling the gas into a reservoir, which was kept at a suitable temperature to attain the desired alcohol concentration in the reactant flow. The reaction was followed by analysis of the gases with two on-line chromatographs: one with a TC detector to determine CO, CO_2 and H_2O concentration, and the other with a FI detector for methanol and the other organic products.

The catalysts, either sulfided or after 4 h of catalytic tests, were characterized by temperature programmed reduction (TPR). The TPR measurements were carried out using a conventional apparatus consisting of a flow system connected to a thermal conductivity cell to follow changes in the composition of the reducing gas (15 vol% of H_2 in N_2). The samples were placed into a tubular reactor which was heated at a constant rate (20°C min^{-1}). Water produced was removed with a liquid nitrogen trap at the outlet of the reactor. Thus, the observed signal was related only to H_2 consumption.

3. Results and discussion

3.1. EFFECT OF REACTION CONDITIONS

Fig. 1 shows that over the present catalysts, dimethyl ether, methane and CO_2 production was maximum at the beginning of the reaction and then it decreased gradually. CO_2 and CH_4 are products from methanol decomposition, as it was reported before for sulfided molybdenum catalysts [8]. Indeed, preliminary experiments in the present work showed CO_2 and CH_4 as products from decomposition of 5.0 mol% of CH_3OH in N_2 at temperatures between 180 and 300°C.

Methyl acetate production increased with reaction time, reaching a constant value after 3 h. H_2S was detected in the product stream at the beginning of the reac-

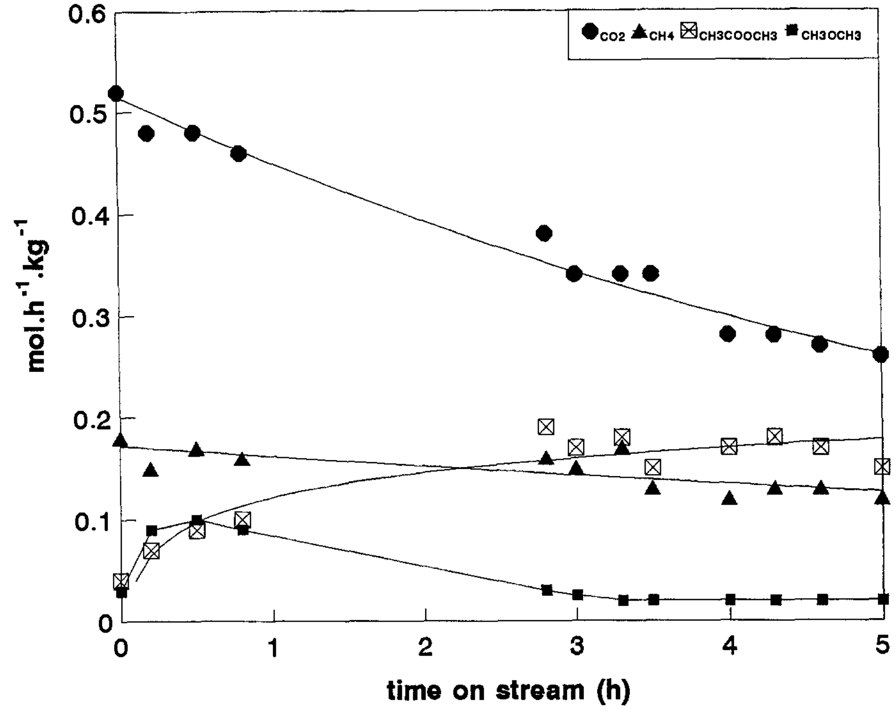

Fig. 1. Rates of formation during methanol carbonylation carried out on sulfided 3/10 CoMo/C catalyst. Reaction conditions: $T = 250°C$; $P = 1$ atm; input %CH_3OH = 5.0 mol%; GHSV = 1000 $\ell\ h^{-1}\ kg^{-1}$. Type of support: Purocarbon.

tion but it was absent at the steady state. This result suggests that a certain catalyst desulfurization is probably involved in the generation of the active sites for methyl acetate production.

Under the reaction condition reported in fig. 1, the selectivity for methyl acetate at steady state was 53 C mol%. This result suggests that the present carbon supported sulfided CoMo catalysts may be promisory for methyl acetate production from the carbonylation of methanol at atmospheric pressure, without requiring methyl iodide as promoter. However, methane production was higher than for other catalytic systems [5].

The steady state selectivity to methyl acetate was found to increase with temperature (fig. 2). A maximum of carbonylation activity was reached at 250°C. Higher temperatures led to a sharp decrease of the carbonylation activity and to an increase of the methane selectivity. Similar results have been found for Ir catalysts, where catalyst deactivation by sintering was reported above 310°C [6].

Production of the ester increased with methanol concentration up to 5 mol% of the alcohol in the reactant mixture (fig. 3). Methane was the main product at a lower concentration of the alcohol in the feed. These results suggest that an adequate partial pressure of methanol over the catalyst is necessary to create and/or

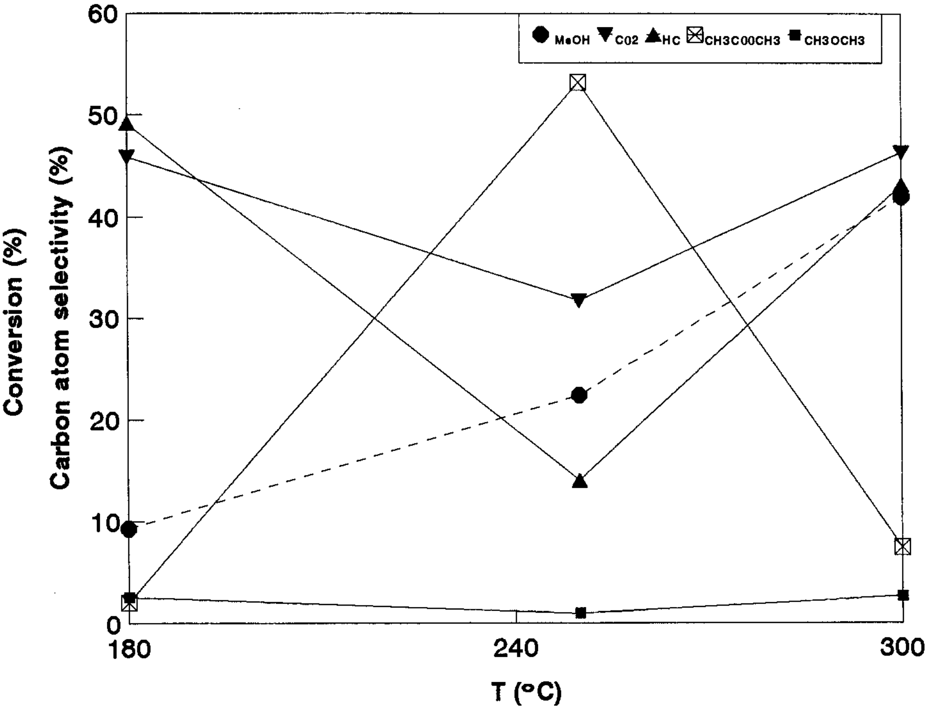

Fig. 2. Effect of temperature on the carbonylation of methanol carried out on sulfided 3/10 CoMo/C catalyst. Other experimental conditions as in fig. 1.

mantain the carbonylation active sites, otherwise methanation is the dominant reaction.

Hydrogen in the reactant flow had an undesirable effect on the selectivity to oxygenates (fig. 4). Methyl acetate and dimethyl ether production decreased as the H_2/CO ratio was increased. This is probably due to reduction of the catalyst, which leads to hydrocarbons formation. Ethanol was found among the products when hydrogen is present. However, the yield of this alcohol in the present work was relatively small as compared to similar catalytic systems reported elsewhere [9,10], suggesting that methanol homologation is not favored over the present catalyst, and that ethanol is probably a product of methyl acetate hydrogenation.

3.2. EFFECT OF Co/Mo COMPOSITION

Table 1 shows the effect of Co and Mo concentrations on the activity and selectivity of the present carbon supported catalysts. Co loadings between 3 and 30 wt% had no effect on methanol conversion and selectivity of the catalysts with 10 wt% of Mo content. Cobalt catalysts (3/0, 30/0) were active for methanol carbonylation, and their selectivities to methyl acetate were similar to the observed for the respective CoMo catalysts (3/10, 30/10). However, methanol conversion was sig-

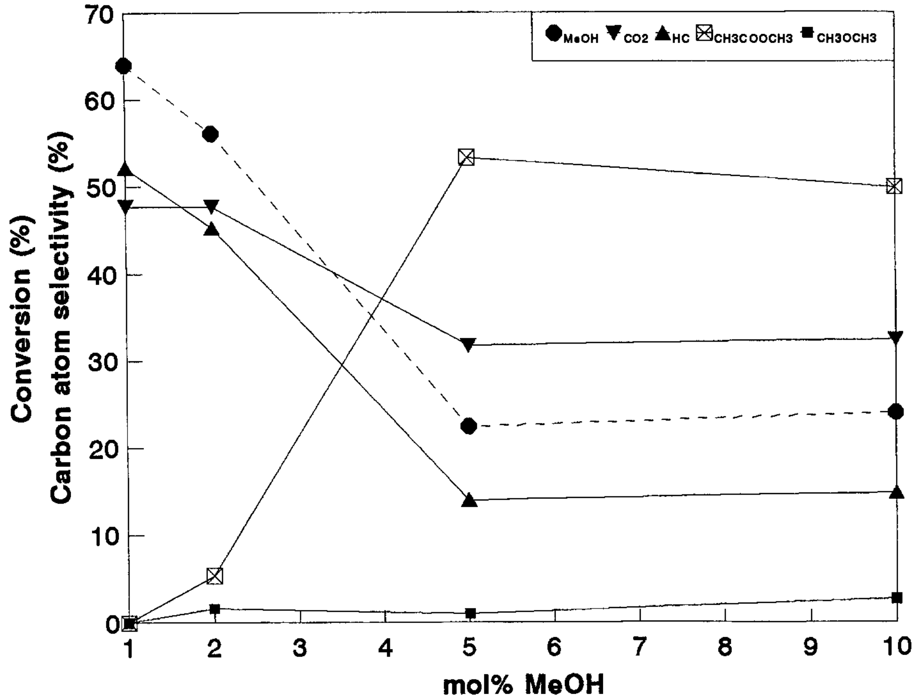

Fig. 3. Influence of alcohol concentration on the carbonylation of methanol over sulfided 3/10 CoMo/C catalyst. Other experimental conditions as in fig. 1.

nificantly higher in the latter. On the other hand, Mo catalysts (0/10) revealed high catalytic activity for methane synthesis, while no methyl acetate was formed.

A scheme of methanol carbonylation reported in the literature [1] suggests that the initial step is the formation of a methyl–metal complex which is believed to be rapidly transformed into an acetyl–metal complex. In accordance with this scheme, the above results suggest that molybdenum is the site where methyl fragments are formed through methanol decomposition. For methyl acetate production, these methyl groups have to migrate to active sites involving cobalt atoms.

For Co containing catalysts, methanol conversion increased with molybdenum content. Small amounts of Mo in the cobalt catalyst led to a significant drop of the methyl acetate selectivity together with an increase in methane production. A highly dispersed molybdenum in the catalyst could enhance hydrogenation of methyl groups since their migration to cobalt sites is less favored. As the content of Mo in the catalyst increases, the presence of a sulfided cobalt phase associated with molybdenum enhances migration of methyl fragments to cobalt sites and then production of the ester.

Selected TPR spectra of sulfided CoMo catalysts are shown in fig. 5. Reducibility of the catalysts was improved when Co content was increased from 3 to 30 wt%. After the catalysts have been used for 4 h the catalysts showed a similar

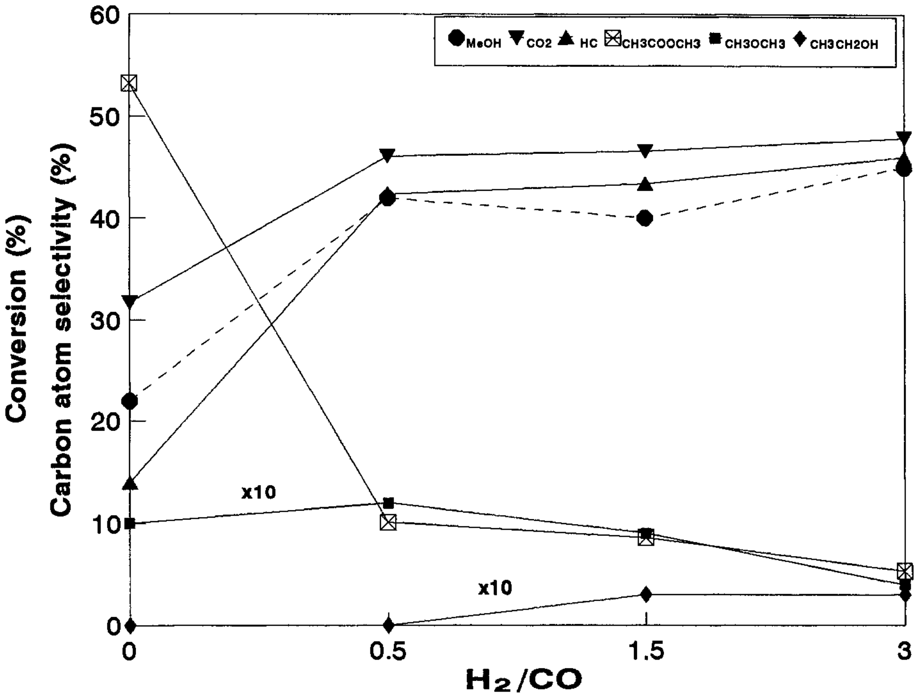

Fig. 4. Effect of input hydrogen concentration on the carbonylation of methanol over sulfided 3/10 CoMo/C catalyst. Other conditions as in fig. 1.

Table 1
Reaction of methanol with CO over carbon supported sulfided catalysts with different cobalt and molybdenum contents [a]

Co/Mo	MeOH conversion (%)	Carbon atom selectivity (mol%)				
		CO_2	CH_4	hydrocarbons C_2–C_3	CH_3COOCH_3	CH_3OCH_3
0/10	62.2	46.3	52.3	1.2	–	–
1/10	61.8	49.3	48.8	0.8	0.6	0.2
3/10	22.4	31.7	12.9	1.1	53.2	1.0
10/10	24.6	32.0	13.8	1.4	52.0	0.7
30/10	22.3	31.8	13.2	1.2	51.9	1.7
30/0	14.0	32.9	15.5	0.8	49.5	1.2
3/0	8.2	32.4	14.5	1.2	50.3	1.4
3/1	18.7	45.5	41.0	1.4	11.2	0.6
3/5	25.6	43.8	37.1	1.2	17.0	0.8
3/10	22.4	31.7	12.9	1.1	53.2	1.0
3/20	31.4	33.8	17.1	1.3	46.1	1.5

[a] Reaction conditions: $T = 250°C$; $P = 1$ atm; $\%CH_3OH = 5.0$ mol%; GHSV $= 1000\ \ell\ h^{-1}\ kg^{-1}$; time on stream: 300 min. Type of support: Purocarbon.

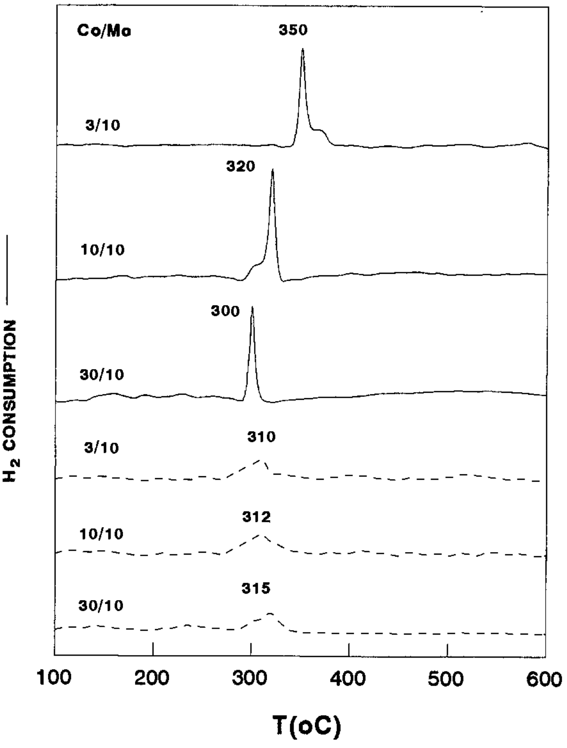

Fig. 5. TPR spectra of selected sulfided CoMo catalysts. Dashed line spectra are after 4 h or use in methanol carbonylation.

TPR signal near 310°C (fig. 5, dashed lines). This result suggests that these catalysts were transformed during reaction to a similar active phase, where methanol carbonylation takes place. That could be the reason for the constant selectivity observed when varying Co loading from 3 to 30 wt% in the catalysts (table 1). It can be speculated that the sulfided cobalt phase present in the 3/10 CoMo catalyst will be the limiting one, from which active sites for methyl acetate production will be created. Partial desulfurization should mark the transformation of the catalysts, as it was also related with the increase of methyl acetate production (see above), indicating that the reaction generates its own active sites for methyl acetate production.

3.3. EFFECT OF THE SUPPORT

Table 2 shows the effect of different carbon supports on the activity and selectivity of the 3/10 CoMo catalyst. Methyl acetate selectivity increased with decreasing carbon surface pH. Different surface properties of the various supports employed are probably the reason for the tendency observed. In a previous work [11], it has been demonstrated that Purocarbon presents a more oxidized surface than Pica,

Table 2
Effect of the type of carbon support on the reaction of methanol with CO over sulfided 3/10 CoMo catalysts [a]

	Purocarbon	Merck	Pica
surface area ($m^2\ g^{-1}$)	1330	753	1280
surface pH	5.0	7.0	10.0
ash (wt%)	2.5	<1	3.0
main ash compounds	P	–	K
MeOH conversion (%)	22.4	21.8	48.6
carbon atom selectivity (mol%)			
CO_2	31.7	38.9	44.2
CH_4	12.9	26.8	37.6
hydrocarbons C_2–C_3	1.1	1.5	1.6
CH_3COOCH_3	53.2	29.9	14.8
CH_3OCH_3	1.0	2.8	1.6

[a] Reaction conditions: $T = 250°C$; $P = 1$ atm; $\%CH_3OH = 5.0$ mol%; GHSV = 1000 $\ell\ h^{-1}\ kg^{-1}$; time on stream: 300 min.

and that reactivity to hydrogen is more significant for the former support. For Ni/C catalysts strong metal–support interactions during impregnation have been observed when H_2 adsorption on the support is small, this latter being a characteristic of basic active carbons [12]. In the present case, cobalt species may be more strongly bound to basic sites than to acidic sites, inhibiting the role of cobalt species as a catalyst.

4. Conclusions

Carbon supported sulfided CoMo catalysts were found to be selective for methyl acetate in the carbonylation of methanol at atmospheric pressure without using methyl iodide as promoter. A temperature around 250°C, and methanol concentrations higher than 5 mol% were found optimum for higher methyl acetate production.

No methyl acetate was found over sulfided Mo/C catalysts, while sulfided Co/C catalysts were as effective for ester production as CoMo/C catalysts. However, methanol conversion was higher when Mo was present in the catalysts.

TPR analysis suggested that the initial sulfided CoMo catalyst is transformed during reaction, leading to an active phase of which reducibility and product selectivity appear to be independent of Co content.

A correlation between the pH of the carbon surface and selectivity to methyl acetate was found, indicating that production of the ester is strongly dependent on the nature of the carbon support.

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