

TRANSFORMATION OF ETHENE INTO KETONES BY CO AND H₂ OVER NiMo SULFIDE CATALYSTSZdenek VIT^{1,*}, Jean Louis PORTEFAIX² and Michele BREYSSE³*Institut de Recherches sur la Catalyse, CNRS, 2, Av. A. Einstein, 69 626 Villeurbanne Cedex, France; e-mail: ¹ vit@icpf.cas.cz, ² portefaix@catalyse.univ-lyon1.fr, ³ breysse@ccr.jvssieu.fr*

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The reaction of ethene, CO and H₂ on NiMo sulfide catalysts at 240–290 °C and at 1 MPa gives ethane, diethyl ketone, propyl ethyl ketone, propanal and diethyl sulfide (DES). The support (carbon, alumina, magnesia and zirconia) influenced the activity of catalysts and the ratio between oxygenated and sulfur products. The carbon supported catalyst was the most active, producing the lowest proportion of DES. The overall oxo selectivity was practically constant in a broad range of ethene conversion. Selectivity into the formation of diethyl ketone increased by lowering the reaction temperature and H₂S concentration in the feed. A selectivity of about 25% into diethyl ketone was achieved with a feed containing 0.4% H₂S at 240 °C.

Key words: Oxo synthesis; Diethyl ketone; Ethene; NiMo sulfide catalyst.

Oxo synthesis, catalyzed by homogeneous complexes of Co and Rh is used industrially to produce aldehydes and alcohols. Due to difficult catalyst recovery, numerous attempts, in the laboratory, have been made to perform this reaction with heterogeneous catalysts¹ and different active phases, based mostly on Rh and Co have been tested^{2,3}. It was found that during these studies, the sulfidation of supported Rh and Ni catalysts improved the selectivity of the reaction because of the suppression of side olefin hydrogenation while the hydroformylation function was maintained or improved^{4,5}.

Recently, diethyl ketone formation was observed during ethene hydroformylation over carbon and zeolite supported Rh catalysts at 90–140 °C and atmospheric pressure by Takahashi and co-workers^{6,7} and was suggested that it proceeds by the reaction of two molecules of ethene with each molecule of CO and H₂ besides that of the normal hydroformylation reaction. Similarly, studying ethene hydroformylation over alumina supported NiMo sulfide catalyst at 290 °C and 1 MPa of pressure we found diethyl ketone as the minor component in the reaction products⁸. Further experiments over

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carbon supported and sulfided Rh, Ir and NiMo catalysts proved the ketones formation⁹.

Formation of ketones as the side products of oxo reactions occurs in some cases when a high pressure (30–150 MPa) and stoichiometric excess of olefin is used^{10,11}. However, the procedures leading to ketones as the main product have been studied less frequently due to a lower industrial importance compared to aldehydes or alcohols. Reactions between CO, olefin and alcohol (or water) as hydrogen donors catalyzed by Raney Co or Rh can give 60–100% of ketones but require a high pressure of about 2–50 MPa and subsequent catalyst separation^{11–14}. On the other hand, recent studies performed with supported Rh catalysts by Takahashi *et al.*^{6,7} and with supported NiMo, Rh and Ir catalysts by us^{8,9} showed the easy formation of ketones during ethene hydroformylation under relatively mild conditions. These results suggest this could be a simple route for the preparation of such compounds using syngas, ethene and cheaper NiMo catalyst.

The main purpose of this work is the more detailed study of ethene transformation by a mixture of CO and H₂ over NiMo sulfide catalysts; with respect to the effect of support and experimental conditions used in order to improve the selectivity of reaction into ketones formation. Three oxides (alumina, magnesia and zirconia) and one active carbon were chosen as supports of catalysts for this study.

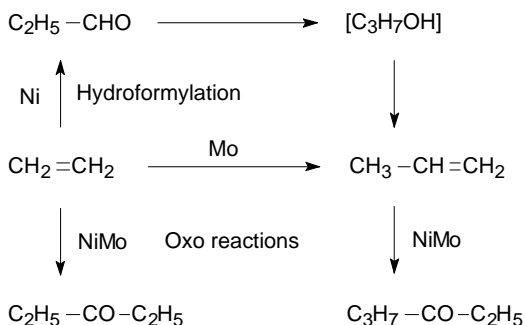
EXPERIMENTAL

Carbon supported NiMo catalyst (2.6% NiO and 15% MoO₃) was prepared from active carbon GA-5 (1 240 m²/g, Slovenské lucobne zavody, Slovak Republic) by the procedure described for the NiMo/C(4) catalyst¹⁵. Magnesia supported NiMo catalyst (3% NiO and 15% MoO₃) was prepared from high surface magnesia (220 m²/g) by impregnation from a non-aqueous solution. The procedure for this preparation is described in detail elsewhere¹⁶ and corresponds to the sample INA(4). The zirconia supported NiMo catalyst (1.8% NiO and 8.5% MoO₃, 130 m²/g) was prepared by Hamon and co-workers¹⁷. Alumina supported NiMo catalyst was a commercial product used in hydrorefining (3% NiO, 14% MoO₃, 220 m²/g). The catalysts (particle size 0.08–0.20 mm) were presulfided in a mixture of H₂S/H₂ (15% H₂S) at 400 °C for 4 h before catalytic tests.

The reaction was carried out in a flow reactor with fixed bed between 240–290 °C at an overall pressure of 1 MPa as described in detail previously^{8,9}. An equimolar mixture of ethene, CO and H₂ with 18.6% N₂ as internal standard and 0.4% H₂S (unless otherwise stated) was passed over the sulfided catalyst. All gases (99.99% purity) were used as received from Alphagaz France. The H₂S was added to the feed in an attempt to keep the catalysts in sulfided state. After the initial decline of activity, usually about 25% during the first 6 h, the activity remained constant for the next 30–40 h. Experimental data discussed in this paper corresponds to the steady state values obtained after at least 6 h on stream. If required, the change of overall ethene conversion, $x(E)$, can be achieved by changing the contact time W/F (kg_{cat} h/mol(E)). Selectivity S was defined as the ratio between ethene conversion into the desired product and $x(E)$, multiplied by a factor 100.

RESULTS AND DISCUSSION

Transformation of ethene, over NiMo sulfide catalysts, with CO and H₂ led to three oxygenated products: diethyl ketone, propyl ethyl ketone and propanal. The oxo reactions were accompanied by extensive ethene hydrogenation and by the formation of smaller amounts of sulfur compounds (mostly diethyl sulfide, DES) originating most probably from H₂S addition to ethene¹⁸. The simplified reaction scheme of the formation of oxygenated compounds is shown in Scheme 1.



SCHEME 1

Propanal was formed most probably by hydroformylation reaction on Ni sites, analogously as on the monometallic Ni sulfide catalysts^{5,8}. However, the amount was much smaller over NiMo catalyst owing to suppressed CO insertion property of Ni in the presence of Mo (ref.⁸). On the other hand, formation of both ketones is specific for the NiMo phase, it was neither observed over Ni nor Mo catalysts under the same experimental conditions⁸ and can hardly be in relation to the CO insertion property of Ni phase. More probably, ketones originate from the reaction of two molecules of olefin with each molecule of CO and H₂, as was similarly suggested earlier by Takahashi *et al.*⁷ in case of carbon supported Rh catalyst. Formation of propyl ethyl ketone *via* intermediate propylene is obviously analogous to that of diethyl ketone; the presence of Mo phase in the NiMo catalyst is probably responsible for the partial transformation of ethene into propylene⁸ while the NiMo phase is probably responsible for the subsequent reaction with ethene, CO and H₂. An additional possible source of propylene could be the dehydration of propanol, which was present in traces among the reaction products.

The effect of support on activity and selectivity of the NiMo catalysts is shown in Fig. 1. Overall activity decreased in the order carbon > alumina > magnesia > zirconia, which is in approximate relation to decreasing surface areas of the supports used. The dominating reaction product was always ethane while the amounts of oxygenated products and DES were substantially lower. Among metal oxide supported catalysts, the support did not significantly influence neither the overall proportion of oxygenated

products nor their composition; the overall oxo selectivity varied a little, between 14–16%, and diethyl ketone was always the dominating oxo product. The amount of oxo products, and particularly that of diethyl ketone, was considerably higher over the NiMo/carbon catalyst than compared to oxide catalysts and, at the same time, the proportion of DES was much lower. Very probably, the higher polarity of metal oxides as compared to carbon contributes to the larger extent of H_2S activation on oxidic supports. Moreover, it is known that mercaptane synthesis from H_2S and olefins is favoured by acidic catalysts¹⁹; the highest content of DES observed over NiMo/alumina catalyst agrees well with relatively higher acidity of alumina compared to zirconia and magnesia. The main difference between carbon and the other three oxide supported NiMo catalysts consists in a lower formation of sulfur compounds and a slightly higher extent of ethene hydrogenation. The overall oxo selectivity was practically the same (13%) compared to oxide supported NiMo catalysts.

The obtained results show, that the formation of diethyl ketone proceeded over all the NiMo catalysts studied, despite the type of support used. This is the interesting difference when compared to Rh catalysts, where diethyl ketone was found only using the carbon and zeolite supported catalysts. The other catalysts prepared by Rh deposition onto silica, alumina, silica–alumina, zirconia or magnesia were not capable of this reaction⁶.

Because the reaction of ethene with CO and H_2 in the presence of H_2S is a complicated reaction system, we attempted to obtain more information about the catalyst selectivity as a function of the overall degree of ethene transformation. Figure 2 shows the effect of contact time on the formation of different reaction products for the NiMo/carbon catalyst, chosen as a typical example. Similar data was also obtained for the other catalysts. The values of ethene conversion into ethane, diethyl ketone and propyl ethyl ketone grew steadily with increasing contact time, whereas the curves for DES and propanal were flat and reached an almost constant value early. The amounts

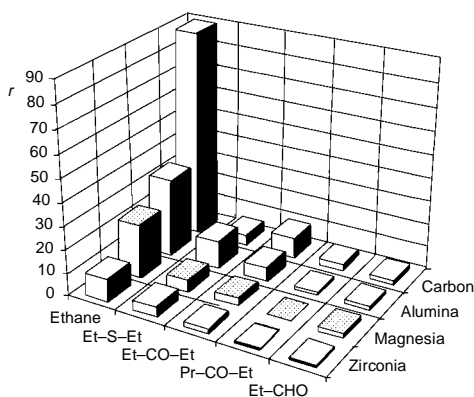


FIG. 1

Effect of support of the NiMo catalysts on the rate of formation r (mol/h kg) of ethane, DES, diethyl ketone, propyl ethyl ketone and propanal (1 MPa, 290 °C, $W/F = 2$ kg h/mol(E), 0.4% H_2S in the feed)

of ethane, diethyl ketone, and in a rough approximation also that of propyl ethyl ketone, increased in a more or less constant ratio. On the other hand, no increment of DES and propanal amounts at the higher values of contact time was observed.

This behaviour can be explained considering the reaction stoichiometry, composition of the feed and different reactivities of the products. As a matter of fact, the amount of DES which can be formed is limited by much lower initial concentrations of H_2S in the feed then compared to ethene. Nevertheless, the value of ethene conversion into DES shown in Fig. 2 corresponds to only 37% of H_2S consumption. We assume, that the remaining part of H_2S is in the adsorption–desorption equilibrium with the catalyst keeping it in sulfided state and probably, some part of H_2S could participate in the formation of higher sulfur products. The apparent cease of propanal formation at the higher values of contact time can be explained by its high reactivity; this compound can easily undergo consecutive transformations by reactions like aldolization²⁰, H_2S addition under dithiole formation²¹ or catalytic decarbonylation²².

Figure 3 shows the effect of overall ethene conversion on the selectivity of NiMo/C catalyst. The most significant changes occur in the early stages of the reaction where the formation of DES dominates for a short time over the formation of oxo products. After this initial period, *i.e.* above the value of ethene conversion of about 0.05, this ratio changed rapidly because of the overwhelming effect of constantly increasing amounts of ethane and both ketones. The catalyst selectivity approached a value, which did not change substantially above the ethene conversion of about 0.25.

The effect of reaction temperature on the selectivity of carbon supported NiMo catalyst is documented by data in Table I. Decrease of reaction temperature from 290 to 240 °C increased the formation of both ketones approximately by 3 times and suppressed the extent of ethene hydrogenation substantially. This is due to the lower activation energies of oxo reactions as compared to ethene hydrogenation⁹. Similar trend

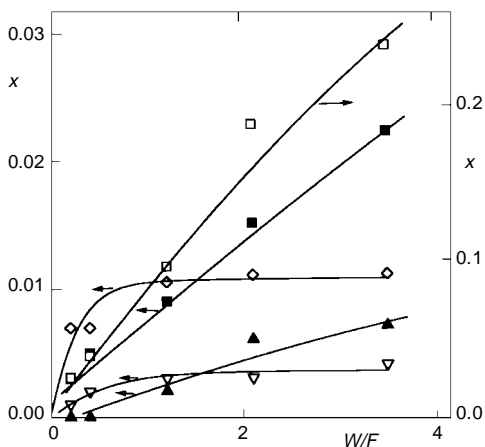


FIG. 2

Effect of contact time W/F on the ethene conversion x into ethane (□), diethyl ketone (■), DES (◇), propyl ethyl ketone (▲) and propanal (▽) over NiMo/carbon catalyst (1 MPa, 290 °C, 0.4% H_2S in the feed)

TABLE I

Effect of reaction temperature on the selectivity of NiMo/carbon catalyst (1 MPa, $W/F = 3.5\text{--}40$ kg h/mol(E), 0.4% H_2S in the feed)

$T, ^\circ\text{C}$	$x(\text{E})$	$S, \%$				
		Et-CO-Et	Pr-CO-Et	Et-CHO	Et-S-Et	Ethane
290	0.29	7.7	2.5	1.4	3.9	84
270	0.41	13.6	6.9	1.5	3.0	75
240	0.40	25.1	10.4	1.5	3.0	60

TABLE II

Effect of H_2S concentration in the feed on the selectivity of NiMo/carbon catalyst (270 $^\circ\text{C}$, 1 MPa, $W/F = 11$ kg h/mol(E))

$\text{H}_2\text{S}, \text{vol.}\%$	$x(\text{E})$	$S, \%$				
		Et-CO-Et	Pr-CO-Et	Et-CHO	Et-S-Et	Ethane
1.6 ^a	0.37	7.0	4.6	1.9	18.5	68
0.4	0.41	13.6	6.9	1.5	3.0	75
0.03	0.57	15.6	3.5	0.7	0.2	80

^a Ethene : CO : $\text{H}_2 = 1 : 1 : 2$.

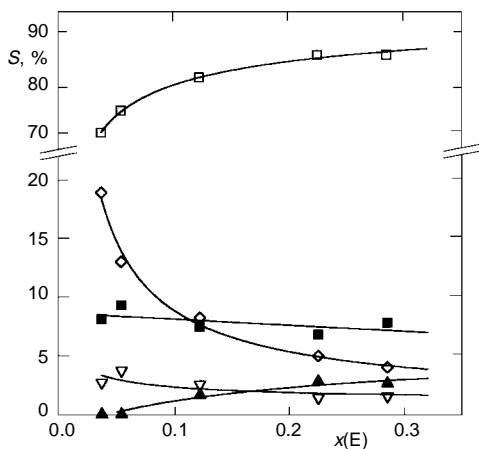


FIG. 3

Effect of overall ethene conversion $x(\text{E})$ on the selectivity S into ethane (□), diethyl ketone (■), DES (◇), propyl ethyl ketone (▲) and propanal (▽) over NiMo/carbon catalyst (1 MPa, 290 $^\circ\text{C}$, 0.4% H_2S in the feed)

was observed for the propanal formation over sulfided CoMo/alumina catalyst⁸ and metallic Rh catalysts^{23,24}. The achieved selectivity over the NiMo sulfide catalyst into diethyl ketone was about 25% which was in the range of that found by Takahashi *et al.*^{6,7} working with carbon supported Rh catalyst (0.5–28%).

The concentration of H₂S in the feed is an important factor affecting the selectivity of NiMo sulfide catalysts. Preliminary experiments with different NiMo catalysts showed that a lowering of H₂S concentration in the feed from 1.6 to 0.4% increased the content of diethyl ketone by approximately 100%. Additional experiment with an H₂S concentration of about 0.03% confirmed this trend. Selectivity of the NiMo/carbon catalyst as a function of different H₂S concentration in the feed is shown in Table II. It is clearly seen, that lowering the H₂S partial pressure facilitates diethyl ketone formation and ethene hydrogenation. An interesting feature of these experiments was the fast and reversible response in catalyst selectivity following the change of H₂S concentration. From this behaviour it follows that catalyst selectivity is closely related to adsorption–desorption equilibrium between H₂S and NiMo phase; an increase of H₂S partial pressure leads to increased chemisorption and therefore to the higher occupation of Mo vacancies which are required for ethene hydrogenation. As can be seen from data in Table II, diethyl ketone formation is obviously parallel to this trend. Its formation was observed only on the NiMo catalysts instead of monometallic Ni and Mo; at the same time, the NiMo/alumina catalyst displayed a distinct synergism between Ni and Mo in ethene hydrogenation and DES formation⁸. Therefore it seems, that the ketones formation proceeds exclusively on the supported catalysts with a high hydrogenation function thus explaining why it was only observed, up to now, on catalysts like Rh, Ir or NiMo sulfide phase.

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