Ketones formation during ethylene hydroformylation over sulfided Rh, Ir and NiMo carbon supported catalysts

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While studying the hydroformylation of ethylene over different carbon supported sulfided catalysts, we observed an interesting property of Rh, Ir and mainly NiMo to form ketones. This could be a simple way for preparing such molecules from syngas using a cheaper catalyst and under milder reaction conditions than those usually employed.

Keywords: ketones formation; hydroformylation; ethylene; sulfide catalysts; carbon support

1. Introduction

The formation of ketones during propylene hydroformylation over RhNaX and RhNaY zeolites has been reported for the first time by Rode et al. [1], who suggested that such a formation proceeds by a consecutive reaction of the primary product, butanal, with the olefin on the zeolite support. Similarly, Takahashi et al. [2,3] have observed the formation of diethylketone beside that of propanal during ethylene hydroformylation over carbon supported Rh catalysts; this diethylketone formation was explained by a direct reaction of two molecules of ethylene with one molecule CO and one molecule H_2.

More recently, during a study of the hydroformylation of ethylene over different carbon supported sulfided catalysts, we observed such ketone formation reactions occurring not only over Rh containing solid, but also over some other solids studied, namely Ir and NiMo catalysts. These results are reported in this paper.

2. Experimental

The preparation of the precursors of the carbon supported Rh and Ir catalysts

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was described in ref. [4]. The carbon supported NiMo catalyst precursor was the same as used in ref. [5], denoted then as NiMo/C4. These precursors (particle size 0.08–0.20 mm) were sulfided under a mixture of H_2S/H_2 (15% H_2S) at 673 K for 4 h. For comparison with the previous work by Takahashi et al., the Rh/C precursor was also reduced under H_2 at 673 K for 2 h.

The contents of sulfur and metals in the catalysts were determined by coulometric titration of SO_2 after catalyst oxidation and by X-ray fluorescence spectrometry, respectively.

The hydroformylation reaction was carried out in a stainless steel flow reactor with fixed bed at 563 K and under a total pressure of 10^6 Pa, as described in detail elsewhere [6]. The feed contained an equimolar mixture of ethylene, CO and H_2 (27% : 27% : 27%) with 0.4% of H_2S and 18.6% of N_2 as internal standard. H_2S was added to the feed in order to keep the catalysts in the fully sulfided state during the hydroformylation reaction. Ethylene, CO, H_2, H_2S and N_2 were used as received from Alphagaz France.

The reaction products were identified on a GC-9A gas chromatograph coupled with a mass spectrometer QP-1000 (Shimadzu) using a capillary Poraplot Q column (20 m) and a temperature program from 40 to 513 K. On line GC analyses of the feed and of the reaction products were performed on a 3.5 m Carbosphere column at 443 K by TCD detection (CO, ethylene, ethane) and on a 3.5 m Porapak R column at 443 K by FID detection (propanal, diethylketone, propylethylketone and diethylsulfide).

The catalysts lose usually 25% of activity during the first 4–6 h on stream. After this initial period, their performances are practically constant during the additional 30 h. The activities of the catalysts were calculated from the composition of the gas phase at the outlet of the reactor when this steady state was reached. During catalytic tests, apparent activation energies for Et–CO–Et, Pr–CO–Et and ethane formation were estimated at about 48, 31 and 130 kJ/mol, respectively, in agreement with literature data [3].

3. Results and discussion

Metal loading and metal-to-sulfur ratio of the catalysts after sulfidation are given in table 1. The atomic ratio S/Me suggests that Rh and Ir catalysts are com-

Table 1
Metal loading and sulfur-to-metal ratio (S/Me) of catalysts after sulfidation

Catalyst	Metal loading (wt%)	S/Me
Rh/carbon	8.0	1.69
Ir/carbon	12.9	1.83
NiMo/carbon	2.5 + 10.6	1.89

Table 2
Activity of reduced Rh catalyst. 290°C, 10 atm, catalyst weight 0.1 g. Ethylene : CO : H_2 : N_2 : H_2S = 20 : 20 : 20 : 13 : 0.2 (ml/min)

Catalyst	Rate of formation (mol/h kg)				
	Et–CHO	Et–CO–Et	Pr–CO–Et	ethane	Et–S–Et
Rh/carbon	10.0	1.0	1.0	104	4.2

posed mostly of Rh_2S_3 [7] and IrS_2 phases, respectively. The S/Me value determined for NiMo/carbon catalyst after sulfidation at 673 K for 4 h is close to that obtained by calculation assuming that the catalytic phase is composed of NiS and MoS_2.

Results of catalytic tests with the carbon supported reduced Rh catalyst are shown in table 2. This catalyst produces diethylketone and propylethylketone in addition to propanol and ethane. The presence of diethylketone is in agreement with observations of Takahashi et al. [2,3] but propylethylketone is a new product which was not observed up to now, suggesting a more complicated reaction pathway of ethylene transformation during hydroformylation. It should be noted here that diethylsulfide was always present in our reaction products; it is probably originating from the addition to ethylene of the H_2S present in the feed.

A comparison of carbon supported and sulfided Rh, Ir and NiMo catalysts is shown in table 3. The formation of the normal hydroformylation product, propanal, was highest over the Rh catalyst. The Ir catalyst produced much less propanal and more ethane, similarly as obtained with the same active phase supported on silica [8,9]. Moreover, the Ir catalyst produced higher amounts of ketones in comparison to the Rh catalyst. The NiMo catalyst, although not belonging to the noble metal family, produced a comparable amount of propanal as in the case of the Ir catalyst, but a much higher amount of ketones. The extent of ethylene hydrogenation over the NiMo catalyst was lower as compared to both Rh and Ir catalysts, so its overall oxo selectivity achieved 13% in contrast to Rh and Ir catalysts where it was 7 and 2%, respectively. Diethylketone was clearly the prevailing oxo product over the NiMo catalyst. In a previous work concerning alumina supported sulfided

Table 3
Activity of sulfided Rh, Ir and NiMo catalysts. 290°C, 10 atm, catalyst weight 0.1 g. Ethylene : CO : H_2 : N_2 : H_2S = 20 : 20 : 20 : 13 : 0.2 (ml/min)

Catalyst	Rate of formation (mol/h kg)				
	Et–CHO	Et–CO–Et	Pr–CO–Et	ethane	Et–S–Et
Rh/carbon	8.5	0	2.4	123	4.2
Ir/carbon	1.4	2.8	2.4	346	1.4
NiMo/carbon	1.7	7.1	2.4	71	4.3

catalysts [6], we also observed some diethylketone formation over the NiMo active phase; but it is worth mentioning that such a formation of ketones seems to be specific of the NiMo phase since neither Ni nor Mo alone were capable of this reaction.

Diethylketone formed during hydroformylation seems to be the result of the reaction of two molecules of ethylene with one molecule of CO and one of H_2 as suggested earlier [2,3].

It is more complicated to explain the presence of propylethylketone, because propylene was not fed into the reactor as starting material. During experiments with Mo/alumina sulfide catalyst performed earlier [6], we found a significant amount of propylene (up to 15%) in the reaction products. It has been previously reported that, in the presence of metallic Mo catalyst, ethylene can be transformed into higher olefins [10]. We may suppose that in our case propylene is formed by ethylene homologation on the coordinatively unsaturated molybdenum sites present in the sulfided NiMo catalyst. Then the formation of propylethylketone can be explained easily considering a pathway similar to that proposed for ethylene:

$$CH_3{-}CH{=}CH_2 + CH_2{=}CH_2 + CO + H_2 \rightarrow Pr{-}CO{-}Et\,. \qquad (1)$$

In the case of Rh and Ir catalyst, however, some other sources of propylene must exist, because, as far as we know, homologation ability toward olefins has not been reported for these catalysts. Nevertheless, because traces of propanol were present among the reaction products, we suppose that propylene can also be formed by its dehydration,

$$Et{-}CHO + H_2 \rightarrow Pr{-}OH \rightarrow CH_3{-}CH{=}CH_2 + H_2O\,, \qquad (2)$$

and then gives propylethylketone according to eq. (1).

4. Conclusion

The present results show an interesting property of sulfided Rh, Ir and NiMo carbon supported catalysts to form ketones from ethylene, CO and H_2. Selectivity to formation of ketones was found higher for the NiMo catalysts than for Rh and Ir catalysts. This could be a simple method for preparation of ketones from syngas using a cheaper catalyst under milder reaction conditions by comparison to conventional methods, i.e. dehydrogenation of alcohols, catalytic transformation of propionic acid over thoria [11] or syntheses using Raney Co catalysts at high pressures of about 2×10^7 to 5×10^7 Pa [12].

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References

[1] E. Rode, M.E. Davis and B.E. Hanson, J. Chem. Soc. Chem. Commun. (1985) 716.
[2] N. Takahashi, H. Arakawa, A. Kano, Y. Fukagawa and K. Asao, Chem. Lett. (1990) 205.
[3] N. Takahashi, T. Takeyama, T. Yanagibashi and U. Takada, J. Catal. 136 (1992) 531.
[4] Z. Vit and M. Zdrazil, J. Catal. 119 (1989) 1.
[5] E. Hillerova and M. Zdrazil, Catal. Lett. 8 (1991) 215.
[6] Z. Vit, J.L. Portefaix and M. Breysse, Appl. Catal. 116 (1994) 259.
[7] M. Lacroix, N. Boutarfa, C. Guillard, M. Vrinat and M. Breysse, J. Catal. 120 (1989) 473.
[8] S.S.C. Chuang, Appl. Catal. 66 (1990) L1.
[9] K. Takeuchi, T. Hanaoka, T. Matsuzaki, M. Reinikainen and Y. Sugi, Catal. Lett. 8 (1991) 253.
[10] T. Nakamura, M. Yamada and T. Yamagushi, Appl. Catal. 87 (1992) 69.
[11] BASF, 2111722 (1971).
[12] G. Natta, P. Pino and R. Ercoli, J. Am. Chem. Soc. 74 (1952) 4496.