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Abstract

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HYDROGENATION OF FURAN COMPOUNDS ON A SKELETAL Cu–Al CATALYST

Copper catalysts, especially copper chromite, have been used rather widely for the hydrogenation of furan compounds. The ability of these catalysts readily to hydrogenate an olefinic bond and a carbonyl group without affecting the furan ring makes it possible to use them for the selective reduction of furan compounds containing various unsaturated bonds in the molecule. The field of application of copper catalysts in hydrogenation reactions of compounds of the furan series was limited mainly by the conditions of carrying out the reaction in the liquid phase. Furfural, silvan, furfuryl alcohol, furfurylidene ketones, and many other furan compounds on copper chromite either were reduced to more saturated furan compounds or, as a result of hydrogenolysis of the ring, were converted into alcohols and diols of the aliphatic series. In this respect, in contrast to some other catalysts, for example Adams platinum, hydrogenolysis of the ring in silvan and furfuryl alcohol on copper chromite proceeds in both possible directions–along the C–O bonds 1,2 and 1,5 [(1)]. However, hydrogenation of silvan on copper chromite [(2)], and also on skeletal Cu–Al [(3)], in the vapor phase at 275° and normal pressure leads to opening of the ring in only one direction, namely along the C–O bond 1,5. All these facts pose the problem of investigating the influence of pressure and temperature on the sequence of reduction of unsaturated bonds in various compounds of the furan series. In the present work the action of these factors was studied in the hydrogenation of furan compounds on a skeletal Cu–Al catalyst.

1. The investigation showed that the decisive role of pressure is manifested in the direction of hydrogenolysis of the furan ring. As is known, on skeletal Cu–Al in a flow system at normal pressure the ring in silvan is cleaved exclusively along the C–O bond not adjacent to the methyl group, which leads to the formation of methyl propyl ketone [(3)]:

$$\text{silvan} \xrightarrow{H_2,\ Cu\text{–}Al} CH_3CH_2CH_2C(=O)CH_3$$

If, however, the hydrogenation of silvan is carried out likewise in the vapor phase but at an elevated hydrogen pressure, the furan ring is cleaved in both possible directions along the C–O bonds 1,2 and 1,5, and the relative amounts

of pentan-1-ol and pentan-2-ol thereby formed change noticeably depending on the magnitude of the pressure applied. Thus, at 250° and 50 atm hydrogen pressure, 41% pentan-1-ol and 44% pentan-2-ol are formed, while at 25 atm and the same temperature, 33% pentan-1-ol and 54% pentan-2-ol are formed:

$$\text{silvan} \xrightarrow[250^\circ]{H_2,\ Cu\text{–}Al} \begin{matrix} CH_3CH_2CH_2CH_2CH_2OH \\ CH_3CH_2CH_2CH(OH)CH_3 \end{matrix}$$

Increasing the temperature favors, on the one hand, dehydrogenation of pentan-2-ol to methyl propyl ketone and, on the other, deeper cleavage of silvan with formation of *n*-pentane and water. At 340–350° and 50 atm, about 30% *n*-pentane, 12% methyl propyl ketone, 20% pentan-1-ol, and 24% pentan-2-ol are formed. In addition, in all cases hydrogenation of silvan at elevated hydrogen pressure gave tetrahydrosilvan in 5–8% yield. As is known, at normal pressure tetrahydrosilvan is not formed in the presence of this catalyst.

2. In the hydrogenation of alkylfurylcarbinols on skeletal Cu—Al under conditions of both normal and elevated hydrogen pressure, the primary reaction is reduction of the hydroxyl group and conversion of the alkylfurylcarbinols into the corresponding α-alkylfurans. At normal pressure and 230–250°, α-alkylfurans can be obtained in yields of up to 95%:

$$\text{furyl-CH(OH)-CH2CH3} \xrightarrow[230\text{-}250^\circ]{H_2,\,Cu-Al} \text{furyl-CH2CH2CH3} + H_2O$$

Subsequent hydrogenolysis of the ring, which becomes more noticeable at elevated temperatures, leads to the formation of aliphatic ketones. However, such high selectivity with respect to reduction of the hydroxyl group while preserving the furan ring is not observed in hydrogenation under elevated hydrogen pressure. Under these conditions, hydrogenolysis of the ring proceeds much more intensively in two directions, and the reaction products contain, along with α-alkylfurans, aliphatic alcohols and a small amount of α-alkyltetrahydrofurans. For example, as a result of hydrogenation of ethyl-α-furylcarbinol in a flow system at 250° and 50 atm hydrogen pressure, 22% α-*n*-propylfuran, 10% α-*n*-propyltetrahydrofuran, 24% heptan-1-ol, and 25% heptan-4-ol are formed:

$$\text{furyl-CH(OH)-CH2CH3} \xrightarrow[250^\circ,\ 50\ \text{atm}]{H_2,\,Cu-Al} \text{furyl-CH2CH2CH3} \longrightarrow \text{tetrahydrofuryl-CH2CH2CH3}$$

$$\text{furyl-CH2CH2CH3} \xrightarrow{\text{ring hydrogenolysis}} \text{heptan-1-ol} + \text{heptan-4-ol}$$

3. In alkyl-α-furyl ketones, as in alkyl-α-furylcarbinols, primary reduction of the carbonyl group with preservation of the furan ring is possible in

the vapor phase. The catalyst for this reaction is, for example, nickel deposited on zinc or cadmium oxides (4), but another sequence of reactions is also possible: reduction of the carbonyl group and hydrogenolysis of the furan ring. Thus, on platinized carbon in the vapor phase at normal pressure, before reduction of the carbonyl group in α-methyl-α'-acetylfuran, hydrogenolysis of the furan ring occurs at the C–O bond adjacent to the carbonyl group; moreover, the products of hydrogenolysis formed initially undergo further transformations with formation of six-membered oxygen-containing carbocyclic compounds (5).

The skeletal Cu–Al catalyst in the hydrogenation reaction of alkylfuryl ketones in the vapor phase at normal pressure behaves analogously to nickel catalysts, i.e., it first reduces the carbonyl group without affecting the furan ring, but it is distinguished by considerably higher selectivity. For example, 2-methyl-5-acetylfuran is reduced at 230–250° to 2-methyl-5-ethylfuran in 90–95% yield:

$$\text{2-methyl-5-acetylfuran} \xrightarrow[230\text{-}250^\circ]{H_2,\ Cu-Al} \text{2-methyl-5-ethylfuran} + H_2O$$

The use of increased hydrogen pressure here, as in the case of alkylfurylcarbinols, sharply decreases the selectivity of reduction of the carbonyl group, since it promotes, to a very considerable extent, hydrogenolysis of the furan ring:

$$CH_3{-}\text{furyl}{-}C(=O){-}CH_3 \xrightarrow[250^\circ,\ 50\ \text{atm.}]{H_2,\ Cu-Al} CH_3{-}\text{furyl}{-}CH_2CH_3 \longrightarrow CH_2{-}\text{tetrahydrofuryl}{-}CH_2CH_3$$

$$\left.\begin{matrix}\text{heptanol-2}\\ \text{heptanol-3}\end{matrix}\right\}40\%$$

4. Skeletal Cu–Al catalyst showed high activity and selectivity in the reduction, in the liquid phase, of furfurylidene ketones and α-alkyl-β-furylacroleins to the corresponding furan alcohols. At 120–140°, 1-α-furylalkanols-3 were obtained in 90–95% yield, and 2-alkyl-3-α-furylpropanols-1 in 75–85% yield:

$$\text{furyl}{-}CH{=}CH{-}C(=O){-}R \xrightarrow[130^\circ,\ 50{-}150\ \text{atm.}]{H_2,\ Cu-Al} \text{furyl}{-}CH_2CH_2{-}CH(OH){-}R$$

$$R = CH_3,\ C_2H_5,\ \text{n}{-}C_3H_7$$

$$\text{furyl}{-}CH{=}C(R){-}CHO \longrightarrow \text{furyl}{-}CH_2{-}CH(R){-}CH_2OH$$

$$R = CH_3,\ C_2H_5,\ \text{n}{-}C_3H_7$$

From the hydrogenation products of α-alkyl-β-furylacroleins, 3-methyl-1,6-dioxaspiro-(4,4)-nonane and 3-ethyl-1,6-dioxaspiro-(4,4)-nonane were isolated in yields of 12–20%. The physical properties of the furan alcohols and spirans obtained by us are given in Table 1 (for literature data see the work of A. Ponomarev[6]).

Table 1

Properties of alcohols of the furan series and spirans

Hydrogenation products	B.p., °C	d_4^{20}	n_D^{20}
1-α-Furylbutanol-3	67–69 (4)	1.0202	1.4754
1-α-Furylpentanol-3	77–78 (4)	1.0023	1.4750
1-α-Furylhexanol-3	97–98 (5)	0.9861	1.4707
1-α-Furyl-2-methylpentanol-3*	84–85 (5)	0.9928	1.4738
2-Methyl-3-α-furylpropanol-1	72–74 (4)	1.0243	1.4785
2-Ethyl-3-α-furylpropanol-1	80–83 (3)	1.0059	1.4797
2-iso-Propyl-3-α-furylpropanol-1	97–100 (4)	1.0013	1.4846
3-Methyl-1,6-dioxaspiro-(4,4)-nonane	58.5–60 (15)	0.9966	1.4452
3-Ethyl-1,6-dioxaspiro-(4,4)-nonane	49–50.5 (4)	0.9788	1.4489

* In DAN, 128, 946 (1959), through an oversight by the authors, the constants of 1-(α-furyl)-2-methylpenten-1-one-3 were erroneously given for this compound.

Thus, the results of the present investigation show that the use of increased pressure in the hydrogenation of α-alkylfurans over skeletal Cu–Al in a flow

system makes it possible to carry out hydrogenolysis of the furan ring in two directions, with formation of primary and secondary aliphatic alcohols. Normal pressure is the best condition for the selective reduction of alkylfurylcarbinols and al-

alkyl furyl ketones into the corresponding α-alkylfurans in a flow system over skeletal Cu–Al catalyst. Skeletal Cu–Al has higher selectivity than copper chromite in the reaction of liquid-phase reduction of furfurylidene ketones and α-alkyl-β-furylacroleins to the corresponding furan alcohols.

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REFERENCES CITED

1. R. Connor, H. Adkins, *J. Am. Chem. Soc.*, **54**, 4678 (1932).
2. N. I. Shuikin, I. F. Belskii, DAN, **115**, 330 (1957).
3. N. I. Shuikin, I. F. Belskii, DAN, **125**, 345 (1959).
4. N. I. Shuikin, I. F. Belskii, ZhOKh, **29**, 1096 (1959).
5. N. I. Shuikin, I. F. Belskii, DAN, **127**, 359 (1959).
6. A. A. Ponomarev et al., DAN, **93**, 297 (1953).

Note: Figure translations are in progress. See original paper for figures.