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LETTER TO THE EDITOR

Comment on “Dehydrogenation of Cyclohexanol on Copper Containing Catalysts. I. The Influence of the Oxidation State of Copper on the Activity of Copper Sites” by V. Z. Fridman and A. A. Davydov (*J. Catal.* **195**, 20 (2000))

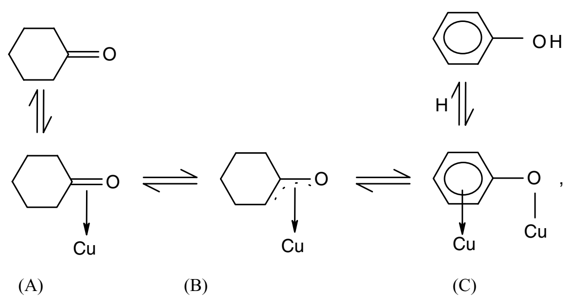
Fridman and Davydov reported in the above paper on their studies on cyclohexanol conversion over Cu–MgO, Cu–ZnO, and Cu–ZnO/Al_2O_3 catalyst (1).

This valuable study is focused mainly on the selectivity of different oxidation states of copper sites toward the formation of cyclohexanone and phenol. The authors came to the conclusion—based on XPS data and FTIR measurements of CO adsorption—that phenol formation was catalyzed only by metallic Cu, whereas both zerovalent and monovalent sites were active in the cyclohexanol–cyclohexanone conversion.

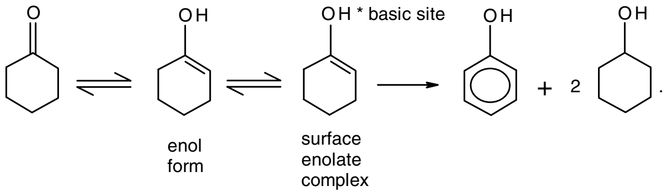
The authors remark in the Introduction of their paper that “. . . the mechanisms of the main reaction of ketone synthesis and aromatization of cyclohexanol are not fully understandable.” Results of their study help to clarify important details in the mechanism of phenol formation from cyclohexanol. The authors disregard, however, the possibility of phenol formation via the cyclohexanone intermediate; this way of phenol formation was indicated and proved first by Swift and Bozik (2). This consecutive route is different from the one depicted in Ref. (1, p. 20) indicating a direct phenol formation from cyclohexanol as a parallel process to cyclohexanone production.

Radiotracer experiments indicated (3) that phenol was formed on metallic copper from cyclohexanol exclusively via cyclohexanone. This conclusion was made on the basis of results obtained during conversion of mixtures of ^{14}C-labeled cyclohexanol and nonradioactive cyclohexanone. The specific radioactivities of the fraction of cyclohexanone and phenol formed during the experiments were nearly equal. A stepwise (cyclohexanol → cyclohexanone → phenol) route was also observed over nickel (3, 4), whereas a direct cyclohexanol conversion to phenol prevailed over the consecutive route on platinum and palladium (3, 5, 6). Cyclohexanol dehydrogenation stopped at cyclohexanone in the presence of other metals (Os, Co, Fe, Ru) of Group 8–10 as well as on Re (6).

The formation of phenol via cyclohexanone raises the question of whether phenol is formed from cyclohexanone (i) due to a stepwise dissociation of C–H bonds in the cycloalkane part of cyclohexanone and hydrogenation of the surface Cu–O bond, as shown in Scheme 1,



or (ii) Via the enol form of cyclohexanone (2), which transforms by dismutation (7) into phenol and cyclohexanol (Scheme 2),



Swift and Bozik explained (2) the promoting effect of added tin oxide on the formation of phenol on Ni/SiO_2 from cyclohexanone with the basic character of tin oxide: promoting enolization and stabilizing the “cyclohexenol” form, followed by easy dehydrogenation of the partially dehydrogenated hydroaromatic ring. Apparently, this was not the case with Fridman’s and Davydov’s catalysts, as, in spite of the substantial differences in the basic character of MgO, ZnO, and ZnO/Al_2O_3 components, the ratio of the maximal phenol/cyclohexanone formation rates (at 300 and 250°C for phenol and cyclohexanone formation, respectively) was almost equal (0.035) for these three types of mixed Cu catalysts. This value was even lower than that (0.055) obtained by calculation from data in Figs. 3 and 4 in Ref. (1) for monometallic Cu. The ratio of the phenol/cyclohexanone formation rate on supported samples

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was also lower than the value measured in our laboratory for metallic Cu catalyst: 0.081 (see data in Table 1).

TABLE 1

Formation Rates of Cyclohexanone (R_c) and Phenol (R_p) from Cyclohexanol on Metallic Cu[a]

t (°C)	R_c (mol/g · min)	R_p (mol/g · min)
220	4.17×10^{-5}	—
250	8.45×10^{-5}	1.07×10^{-6}
280	9.13×10^{-5}	3.25×10^{-6}
300	1.01×10^{-4}	6.82×10^{-6}

[a] Data are seen also in Fig. 1, Ref. (8). Mass of Cu, 1.45 g. Flow rates: cyclohexanol, 3.3 NTP cm^3/min; N_2, 30 NTP cm^3/min.

It should be noted that the phenol/cyclohexanone rate ratio was of the same order of magnitude in Refs. (1, 3) in spite of the substantially different flow rates applied in these studies. This indicates the identity of the reaction mechanism; it supports the consecutivity of phenol formation from cyclohexanol.

The higher ratio of the phenol-to-cyclohexanone formation rate over monometallic Cu than that over Cu–ZnO and Cu–ZnO/Al_2O_3 catalysts and, especially, that in the presence of Cu–MgO of high basicity makes it highly unlikely or even excludes the possibility that enol formation plays a role in the cyclohexanone–phenol step of the conversion. Thus, it follows that Scheme 1 should be accepted as the route of this step of the cyclohexanol–phenol conversion. The exclusion of Scheme 2 is in agreement with the observation (8) that no cyclohexane or benzene was formed on copper from the small amounts of cyclohexene (0.1–0.2 wt%) produced from cyclohexanol via its dehydration. Results of special measurements on cyclohexene conversion, carried out by the method described in Ref. (4), are collected in Table 2. Data in this table indicate that no benzene and only 0.3% cyclohexane was produced from cyclohexene over metallic copper under conditions identical to those applied in the conversion of cyclohexanol.

The rates of phenol formation are substantially lower from cyclohexanone than those from cyclohexanol (8). This and identical observations with other catalysts seemed to indicate that Scheme 1 could not be the only route of the cyclohexanone–phenol step in the cyclohexanol–cyclohexanone–phenol conversion (6). A direct comparison of the conversion of cyclohexanone as a feedstock with that as an intermediate is justified, however, only in the case of equally adsorbed amounts of identical orientation of the feedstock cyclohexanone and that of the intermediate, i.e., an equal adsorption–desorption equilibrium state of cyclohexanone in both cases. In addition, radioactivity measurements demonstrated (3) a substantial net cyclohexanone–cyclohexanol conversion (in N_2 atmosphere too): the original specific radioactivity of cyclohexanol in mixtures of [^{14}C]cyclohexanol and nonradioactive cyclohexanone decreased by ∼40–50% in a 10-min tracer experiment.

TABLE 2

Conversion of Cyclohexene on Cu

t (°C)	Composition (wt%)			
	Cyclohexane	Cyclohexene	Benzene	Unidentified
150	0.03	99.88	—	0.03
200	0.03	99.83	—	0.14
250	0.03	99.73	—	0.24

Note. Mass of Cu, 1.45 g. Flow rates: cyclohexene, 3.3 NTP cm^3/min; N_2, 30 cm^3/min. Length of runs, 10 min.

Consequently, the lower extent of phenol production from cyclohexanone in comparison with that from cyclohexanol must be caused by the parallel cyclohexanone–cyclohexanol conversion and by a possible hindrance in adsorption of suitably oriented cyclohexanone.

The rate of benzene formation from cyclohexane at 300°C was substantially lower on metallic copper, 3.8×10^{-9} mol/g · min (9), than that of phenol formation, as indicated in Table 1. The activation energy of benzene formation was 171 kJ/mol, whereas the activation energy of phenol formation from cyclohexanol was 90 kJ/mol, as calculated from data in Table 1. The higher reactivity of cyclohexanol in aromatization can be explained by the substantially easier C–H bond dissociation due to π–σ conjugation with respect to the C–H(σ)-bond in cyclohexanone, π-bonded to the surface (Scheme 1A), similar to the C–H bond strength in C=C–C–H (i.e., in α-position with respect to a C=C bond), which is lower by ∼90 kJ in comparison with the mean C–H bond strength in hydrocarbons (10). The formation of π-bonded cyclohexanone (Scheme 1A) and its transformation into π-oxoallylic surface species (Scheme 1B) during cyclohexanol conversion was confirmed by IR data (11).

We state in conclusion the following:

- Different from the mechanism depicted by the authors (1), no direct Cu-catalyzed formation of phenol occurs from cyclohexanol; dehydrogenation to cyclohexanone intermediate and its conversion to phenol is the only process of phenol formation from cyclohexanol on metallic copper.
- Comparing the ratio of the phenol/cyclohexanone formation rates obtained by the authors for monometallic Cu with those obtained by them for Cu–MgO, Cu–ZnO, and Cu–ZnO/Al_2O_3 (1) excludes dismutation as a possible way of cyclohexanone–phenol conversion. Presumably the surface π-complex of cyclohexanone intermediate is transformed into phenol via dehydrogenation of the six-member hydrocarbon cycle.

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