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LETTER TO THE EDITOR

Reply to Tétényi and Paál

In their comment (1) on our article (2), Tétényi and Paál remarked that "[r]esults of their study help to clarify important details in the mechanism of phenol formation from cyclohexanol. The authors [Fridman and Davydov] disregard, however, the possibility of phenol formation via the cyclohexanone intermediate . . ." In our study, we did not intend to investigate the mechanism and the intermediate in the formation of phenol from cyclohexanol. As Tétényi and Paál pointed out (1), our study (2) was focused mainly on the reactivity and selectivity of the different oxidation states of copper sites in the formation of cyclohexanone and phenol. Another purpose was to show that the development of a copper catalyst with monometallic copper as the main active ingredient would not lead to a process with high conversion of cyclohexanol and high selectivity. The reason is that at high temperature the active sites simultaneously catalyze the main as well as the side reactions. At the same time we showed that an alternative would be to develop a catalyst with monovalent copper sites. These sites are much more active and selective. The high selectivity of monovalent sites allows operation of this catalyst at higher temperature with high conversion. In spite of the high temperature, the catalyst with monovalent copper will not produce phenol and will provide a high selectivity.

We will discuss our view on the mechanism of cyclohexanone and phenol formation as a follow-up of our former study (2). A more detailed study will be published in due course (4). In (2) we showed a scheme of reactions that occurs in the process of cyclohexanol dehydrogenation. This scheme might suggest that only parallel routes of phenol formation exist. It was presented as general information to show the complexity of the process and the possibility of by-product formation. We did not intend to conclude that there is only one way to form phenol. We agree that it would have been more correct to show also the route of phenol formation via cyclohexanone, but we do not agree with Tétényi and Paál that phenol is formed on metallic copper exclusively from cyclohexanone and we would like to explain why.

From radiotracer experiments, Paál *et al.* concluded that phenol is formed exclusively via cyclohexanone (3). This conclusion was based on an experiment in which a mixture of cyclohexanol and cyclohexanone with initial radioactivities of 1.58 and 0.123, respectively, was dehydrogenated at 300°C on metallic copper. The product contained cyclohexanol, cyclohexanone, and phenol with final radioactivities of 0.97, 1.01, and 0.87, respectively. The authors concluded that because the radioactivity of phenol was not higher than the radioactivity of cyclohexanone (nearly equal), the phenol is formed exclusively from the ketone (3). However, not only are the radioactivities of phenol and cyclohexanone equal, also that of cyclohexanol was nearly equal to that of the other products. Moreover, the radioactivity of cyclohexanol decreased from 1.58 in the initial mixture to 0.97 in the product. The latter observation suggests that there was a fast isotope exchange between cyclohexanone and cyclohexanol on metallic copper that makes these results inconclusive. The second reason for believing that phenol can be formed directly from cyclohexanol is based on our latest IR results of the cyclohexanol and cyclohexanone adsorption on metallic copper. These data will be published in detail in (4), but part of these results are presented in this Reply because it could be useful for understanding the mechanism of the phenol formation on the metallic copper sites.

A Cu–Mg catalyst, prepared as described in (2), with a copper loading of 52 at% was used to study the mechanism of the reaction on zerovalent copper. The IR spectra of adsorbed species were recorded between 25 and 300°C. The details of the method are described elsewhere (5).

With respect to cyclohexanol adsorption on the metallic copper sites, the IR spectrum of the H_2-reduced surface of the Cu–Mg catalyst, after exposure to cyclohexanol at 25°C and subsequent evacuation, does not demonstrate any absorption bands (Fig. 1a). After adsorption of cyclohexanol at 50°C the spectrum displays three absorption bands, at 1590, 1490, and 1300 cm^{-1} in the region 1000–1800 cm^{-1}. These three bands are very similar to the absorption bands in the spectrum of phenol on MgO and CuO (6). The band at 1300 cm^{-1} can be attributed to the C–O stretching in phenol. The bands at 1490 and 1590 cm^{-1} can be assigned to the symmetric and asymmetric stretching of the aromatic bond. These data suggest that cyclohexanol forms a phenollike structure after adsorption on the metallic copper. Moreover, this spectrum shows neither the skeleton C–O–H deformation band at 1370 cm^{-1} nor the OH stretching band at 3500–3550 cm^{-1}, both of which are present in the spectrum of liquid cyclohexanol. Their absence in the spectrum of adsorbed cyclohexanol indicates that cyclohexanol adsorption on metallic copper is accompanied by the breaking

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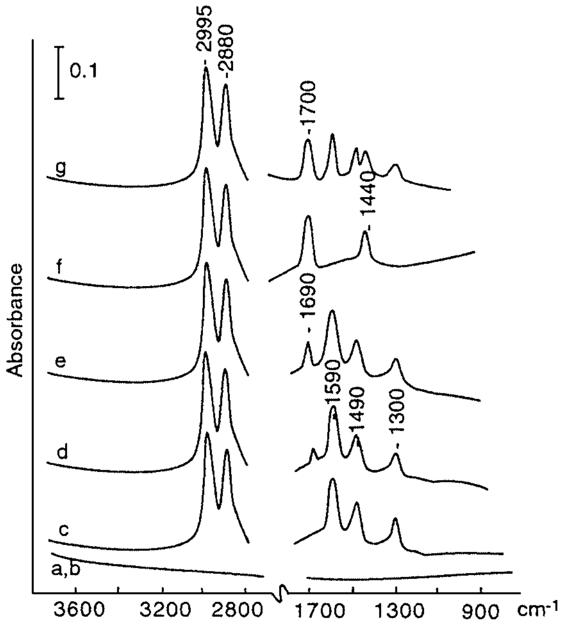

FIG. 1. IR spectra of adsorbed cyclohexanol and cyclohexanone on reduced Cu–Mg catalyst. (a) Initial Cu–Mg catalyst after reduction in H_2 at 250°C and vacuum treatment at the same temperature for 1 h; (b) sample (a) after adsorption of cyclohexanol at 25°C; (c) sample (a) after adsorption of cyclohexanol at 50°C; (d) sample (c) after heating to 200°C; (e) sample (d) after heating to 250°C; (f) sample (a) after adsorption of cyclohexanone at 25°C; (g) sample (f) after heating to 200°C.

of the O–H bond. Furthermore, this spectrum does not show the band at 1070–1100 cm^{-1} that belongs to the C–O stretching in cyclohexanol. At the same time, there are absorption bands at 2880 and 2995 cm^{-1} which can be assigned to the C–H stretching in scissoring CH_2 functional groups (7). The subsequent heating of adsorbed cyclohexanol to 200°C led to the appearance of a band at 1690 cm^{-1}. Increasing the temperature to 250°C increased the intensity of this band, which has been assigned to the C=O stretching in cyclohexanone (7).

Regarding cyclohexanone adsorption on the surface of metallic copper, the spectrum (Fig. 1f) of absorbed cyclohexanone on the Cu–Mg catalyst at 25°C indicates absorption bands that correspond to the bands of liquid cyclohexanone, where the most intensive band is at 1700 cm^{-1}. The subsequent heating of the adsorbed cyclohexanone to 200°C resulted in a decrease of the 1700 cm^{-1} band intensity and the appearance of bands at 1300, 1490, and 1590 cm^{-1}, which, as we believe, also belong to a phenollike structure.

The presented results show that both cyclohexanol and cyclohexanone are able to form a phenollike structure after adsorption on metallic copper, which is ready for the formation of molecular phenol. The formation of the phenollike structure from cyclohexanol occurs at a lower temperature (50°C) than from cyclohexanone (200°C). This is in a good agreement with the observation by Manninger *et al.* (8) that the rate of phenol formation is substantially lower from cyclohexanone than from cyclohexanol (1).

In conclusion, we believe that phenol can be formed simultaneously from cyclohexanol (direct route) and cyclohexanone (consecutive route) in the dehydrogenation of cyclohexanol.

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V. Z. Fridman[1,2]
A. A. Davydov[3]

Reflex Inc. (Catalysis Center,
Research and Consulting)
New York, New York

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[1] To whom correspondence should be addressed.

[2] Present address: Sud-Chemie Inc., 4900 Crittenden Drive, Louisville, KY 40209. E-mail: vfridman@sud-chemieinc.com.

[3] Present address: Syntroleum Corporation, 1350 South Boulder, Suite 1100, Tulsa, OK 74119-3295. Fax: (918) 764-4379. E-mail: adavydov@syntroleum.com.