3. The Na-TsVM and Na-TsVK-1 zeolites, which are practically inactive in ethylene oligomerization and aromatization, manifest high activities in the isomerization and disproportionation of 1-hexene.

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BEHAVIOR OF COPPER-RUTHENIUM CATALYSTS IN ENANTIOSELECTIVE HYDROGENATION

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In skeletal copper-ruthenium catalysts for enantioselective hydrogenation, the active component is the Ru [1], but its properties in these catalysts are much different from the properties that it manifests in an individual Ru catalyst. In this connection, we have investigated analogous Cu-Ru catalysts supported on aerosil (SCRC), modified with R,R-tartaric acid (TA), in the liquid-phase hydrogenation of ethyl acetoacetate (EAA).

## EXPER IMENTAL

The catalysts were prepared by impregnating aerosil (produced by the Kalush Combine, Grade A-300) with aqueous solutions of Cu and Ru chlorides, after which the wet mass was dried and then reduced for 3 h in a stream of  $H_2$  + He. The series A catalysts contained a constant total quantity of metal (10% of catalyst weight) and different Ru:Cu weight ratios (1:9, 2:8, 3:7, 4:6, 5:5, and 10:0). The series B catalysts, with a constant Ru:Cu weight ratio of 1:4, differed in total content of metal (5, 10, 15, 20, 40, and 80% by weight). In the series C catalysts, with an Ru content of 1% by weight, the Cu content was varied from 0 to 14% (at.). The series A and B catalysts were reduced at 450°C, the series C at 500°C, The reduced catalysts were held while mixing for 1 h in a thermostatted (50°) cell with a 0.5% aqueous solution of TA (100 ml of solution per 0.5 g of catalyst). The hydrogenation of the EAA (5 ml per 0.5 g of catalyst) was performed at 90° and 100 atm without any solvent and in ethanol solution (1:1). The catalysate, after removal of the catalyst and distillation, was analyzed by GLC (Khrom-31 instrument, packed glass column, length 3 m, PEG/Chromaton-AW-CMDS, 80°) and spectropolarimetrically (Spektropol-1).

# DISCUSSION OF RESULTS

The hydrogenation of EAA on the series A SCRCs modified at pH proceeds at a rather high rate, both in ethanol solution and without solvent, although in ethanol the hydrogenation rate (v) is about 30% higher. With increasing content of Ru in the SCRC, the activity in-

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Fig. 1. Reaction rate v (1) and optical yield p (2) in hydrogenation of EAA on modified SCRCs, as functions of Ru:Cu ratio in aerosil (in ethanol, series A).



Fig. 2. Reaction rate v (1) and optical yield p (2) in EAA hydrogenation on modified SCRCs as a function of modification pH (without solvent, series A).

Fig. 3. EAA hydorgenation rate v (without solvent) as a function of Cu/Ru atomic ratio (series C).

creases linearly (Fig. 1). The Cu aerosil catalyst is inactive in this reaction, even under more severe conditions (140°, 150 atm). The SCRCs with Ru:Cu ratios of 1:9, 2:8, 3:7, and 4:6 give the optically active product R-(-)-ethyl- $\beta$ -hydroxybutyrate (EHB). On the other SCRC samples and on the Ru/aerosil catalyst, the reaction is nonenantioselective. Thus, with respect to enantioselective hydrogenation, we can see a very definite synergism. Whereas on the individual catalysts Ru/aerosil and Cu/aerosil this reaction does not proceed at all, on the mixed catalysts, the optical yield (p) amounts to 3.5% with a ratio Ru:Cu = 1:9 if the reaction is carried out in the solvent (see Fig. 1).

It is known that enantioselective hydrogenation of EAA can take place on Cu if it is used in the form of a skeletal catalyst [2], in which case the optical yield is 17%. And if the Cu were also active in the Cu-Ru/aerosil catalyst, we could expect manifestation of asymmetrizing properties for this bimetallic catalyst as well. Therefore, since the products obtained on a number of the SCRCs were optically active, we can assume that in this Cu-Ru system, it is specifically such activation of the Cu that takes place, resulting in the appearance of optical activity in the hydrogenated products.

The hypothesis that Cu activity is manifested in SCRCs and that excess R-enantiomer of the EHB is formed specifically on the Cu atoms is in good agreement with the fact that in the modification of the SCRC,  $H^+$  ions have practically the same effect on v and p as in the case of skeletal Cu [2]. An optically active product can be obtained only when the catalyst is modified in the pH region 3-7, and the optimal pH is 5. The pH also has a strong influence on the hydrogenation rate (Fig. 2), the changes in v and p being antibatic. This sort of correlation of values of p and v was also observed in the case of skeletal Cu [2]. From Figs.

TABLE 1. Hydrogenation Rate and Optical Yield in EAA Hydrogenation on Modified SCRCs in Relation to Total Quantity of Metal Supported on Aerosil (series B)

Total wt.% of supported metal Cu + Ru	Optical yield, %	Hydrogenation rate, mmoles/ g cat • h
5 15 20 40	$25 \\ 4,5 \\ 0 \\ 0,2$	1,3 2,1 3,4 1,8

TABLE 2. Catalytic and Asymmetrizing Properties of Modified SCRCs in Relation to Cu/Ru Atomic Ratio

Cu/Ru atomic ratio	Hydrogenation rate, mmoles/ g cat • h	Rate of accumula- tion of excess () - EHB, mmoles/g cat • h	Optical yield, %
0, <b>1</b>	4,5	$\begin{array}{c} 0,45 \cdot 10^{-2} \\ 0,8 \cdot 10^{-2} \\ 5,2 \cdot 10^{-2} \end{array}$	0,1
5,0	2,0		0,4
5,5	0,75		6,9

1 and 2 it can be seen that the hydrogenation of EAA without solvent makes it possible to raise the optical yield from 3.5% to 12% for the SCRC with a ratio Ru:Cu = 1:9.

In the example of the series B catalysts, we found (Table 1) that with a total metal content of 5% by weight, the value of p reaches 25% [3]; as the content of metal in the catalyst is increased, p drops off, first to a few percent and then to zero. With increasing total content of metallic phase in the SCRCs, the values of v pass through a maximum, apparently because of a change in dispersity in this series of SCRCs.

In our investigation of the properties of the series C SCRCs, we found that the catalyst activity depends on the quantity of Cu introduced. The addition of 0.1-1.0% (at.) Cu to the Ru approximately doubles the hydrogenation rate in comparison with the Ru/aerosil catalyst (Fig. 3). Further increases in the Cu content in the series C SCRCs lead to a drop in activity; but in the interval of ratios 4-5, a second activity peak is observed. The SCRCs containing large amounts of Cu (atomic ratio 6.0, 10.0, and 14.0) proved to be inactive.

Spectropolarimetric analysis of the catalysates obtained on the series C SCRCs showed that the only catalysts having enantioselectivity are those corresponding to points on Fig. 3 lying before the first maximum and after the second maximum in activity. The high-activity SCRCs do not give optically active products (Table 2).

From these data it can be seen that, as a rule, SCRCs with high activities give lower values of p or prove to be completely nonenantioselective. This can be explained by competitive hydrogenation of EAA, on the one hand, on dissymmetric centers that presumably consist of Cu atoms and hence should be low in activity, and on the other hand, on nonselective centers that should evidently consist of Ru atoms and should manifest a high activity. This is also the reason for the antibaticity in the variation of p and v when the Ru:Cu ratio or the total amount of metal in the SCRC is varied. Possibly there are different mechanisms of interaction of the Cu and Ru in the SCRCs we have investigated; however, it is clear that, in spite of the lack of any mutual solubility of these metals, they must exist in the supported catalysts in close contact, possibly in bimetallic Cu-Ru clusters [4].

In skeletal copper-ruthenium catalysts, the Cu has a rather strong influence on the properties of the Ru [1]; however, activation of the copper by the ruthenium was not observed. The reason for the observed difference in behavior of these two types of catalyst (skeletal and supported) can be found in the difference between the structures of the active phases of these catalysts. For the skeletal catalysts, on the basis of x-ray phase analysis and adsorption measurements, a two-layer model has been proposed, with the assumption that the

Cu phase is covered by the Ru phase. In the case of SCRCs, apparently, a different model should be proposed, more likely of a cluster nature.

# CONCLUSIONS

1. Synergism has been found in the enantioselective hydrogenation of ethyl acetoacetate on copper-ruthenium catalysts supported on aerosil and modified with (+)-tartaric acid,

2. A hypothesis has been advanced to explain the activating effect of ruthenium on the copper.

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## CHIRODIASTALTIC REACTIONS IN METAL-AMINO ACID-DIKETONE AND METAL-AMINO

## ACID-KETOESTER HETEROLIGAND COMPLEXES

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The asymmetrical hydrogenation of diketones or ketoesters on metal catalysts modified by chiral hydroxy or amino acids proceeds through the formation of an MCS heteroligand complex, where C is the metal catalyst, M is the amino acid or hydroxy acid modifier, and S is the prochiral diketone or  $\beta$ -ketoester substrate [1]. The stereochemical interaction between M and S (or between the [CM] complex and S) in this complex which is termed a chirodiastaltic interaction [2, 3] is manifest in the formation of an optically active product. In the present work, we attempted to obtain a qualitative and quantitative characterization of the chirodiastaltic interactions in heteroligand complexes of copper, nickel, and cobalt which are models for the intermediate complexes of the corresponding metal catalysts in asymmetric hydrogenation.

A study of the circular dichroism (CD) spectra of Cu, Ni, and Co complexes with ethyl acetoacetate (EAA), acetylacetone (AA), methyl acetoacetate (MAA), phenylalanine (Phe), tyrosine (Tyr), and tryptophan (Trp) permitted assignment of the conformation of these complexes and correlate the conformations of the complexes with the optical yields obtained in the asymmetric hydrogenation of these substrates on the Cu, Ni, and Co catalysts modified by the amino acids indicated [4, 5]. The conformation was characterized by the induced circular dichroism ( $\Delta \epsilon$ ) in the absorption band of the dicarbonyl ligand in the complex. The stability constants of the heteroligand complexes were determined spectrophotometrically and potentiometrically [6] and were correlated with the optical yields [7] and the enantioselectivity [8] in the above systems. This suggested the existence of correlations between the dichroic absorption of the complexes and the complex stability constants. This question was examined in the present work.

# RESULTS AND DISCUSSION

The strength of the metal-substrate (C-S) bond upon the formation of the [MCS] complex from  $CS_2$  of  $CM_2$  in a series of monotypic M and S ligands assuming the same nature for the ef-

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