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The Effect of Silica Support Texture and Anion of Impregnating Solution on Ru Dispersion and on Ru–Cu Interaction

In a recent comparative investigation of Ru–Cu and Ru–Ag (*1*) catalysts we believed it advisable to avoid $Ru(Cl)_3$ in the preparation of the Ru–Ag catalyst in order to avoid possible complications of AgCl precipitation. Consequently, we also avoided the use of $Ru(Cl)_3$ in the preparation of our Ru–Cu catalyst so that we might compare the two sets of Ru-group 1B catalysts where all preparation variables were held constant. Our choice of a salt to use in the impregnation of Ru was $Ru(NO)(NO_3)_3$ and for Cu and Ag we used $Cu(NO_3)_2$ and $AgNO_3$, respectively. Our pure Ru catalyst had relatively high dispersion (65% exposed) compared to most previously reported Ru/SiO_2 catalysts (*2–7*). However, our bimetallic catalysts exhibited relatively poor Ru–Cu interaction based on either H_2 chemisorption or suppression of ethane hydrogenolysis compared to that reported earlier by Sinfelt (*2*). In this communication we identify the two dominant preparation variables that account for the difference between our catalysts and those studied by Sinfelt and discuss the nature of these critical preparation variables.

The method of measuring the amount of strong and total H_2 chemisorption was identical to that described previously (*1*). In brief, room temperature isotherms were extrapolated to zero pressure to determine the total chemisorption and a second isotherm (also extrapolated to zero pressure) taken after a 10-min evacuation was subtracted from the first (total) to determine the amount of strong chemisorption. Ethane hydrogenolysis activity was measured in a micro-catalytic pulse reactor by a procedure previously outlined (*8*). Turnover frequencies are based on total hydrogen chemisorption on an assumed H : surface Ru stoichiometry equal to 1.

We have prepared three sets of catalysts. Catalysts A and A′, respectively, are pure Ru and Ru–Cu with a 1 : 1 atomic ratio supported on Cab-O-Sil M5 and prepared from $Ru(Cl)_3$ following the recipe of Sinfelt (*2*). Catalysts C and C′, respectively, are pure Ru and Ru–Cu with a 1 : 1 atomic ratio supported on Davison 923 and prepared from $Ru(NO)(NO_3)_3$ following the recipe of Rouco (*1, 11*). Catalysts B and B′, respectively, were prepared from $RuCl_3$ and supported on Davison 923, i.e., Sinfelt's anion and Rouco's support. All catalysts were 1 wt% Ru. Other than the anion of the Ru salt and the support there were two additional differences in the Sinfelt and Rouco preparations which could be identified: the volume of solution per gram of support (2.2 and 1.0 ml/g, respectively) and the initial reduction temperature (773 and 723 K, respectively). Both of these variables were changed in separate preparations of catalyst B′ and found not to have a substantial effect on the ethane hydrogenolysis activity, i.e., they were judged not to be critical preparation variables in the range of variation used in this study.

Hydrogen chemisorption results are reported in Table 1 and ethane turnover frequencies in Fig. 1. Considering the pure Ru catalyst first, one notes that the micro-porous, high area (600 m^2/g) Davison silica results in a higher dispersion, other variables being held constant, than the relatively low area (200 m^2/g), non-porous Cab-O-Sil. An even higher dispersion is obtained using the combination of high area silica

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TABLE 1

H_2 Chemisorption on Different Ru/SiO_2 and $Ru–Cu/SiO_2$ Catalysts

Catalyst	Support	Salt used	Ru/Cu ratio	H/Ru	
				Strong	Total
A	Cab-O-Sil	$RuCl_3$	1:0	0.10	0.17
B	Davison	$RuCl_3$	1:0	0.21	0.37
C	Davison	$Ru(NO)(NO_3)_3$	1:0	0.36	0.67
A′	Cab-O-Sil	$RuCl_3 + Cu(NO_3)_2$	1:1	0.09	0.18
B′	Davison	$RuCl_3 + Cu(NO_3)_2$	1:1	0.15	0.30
C′	Davison	$Ru(NO)(NO_3)_3 + Cu(NO_3)_2$	1:1	0.45	0.80

and the nitrate anion although not quite as high as obtained by the special preparation described by Gay (*9*). Based on either the total or the strong chemisorption there is little evidence for Ru–Cu interaction and, to the extent that it exists, it appears to result in an increase in H_2 chemisorption rather than a decrease as would have been predicted from Sinfelt's data. We surmise that the difference may be attributed to the procedure used for obtaining the H_2 chemisorption. Apparently Sinfelt has used a period of 30 to 45 min equilibration time for each isotherm point, that being sufficient to reach equilibrium on the non-porous supports (*10*). On the micro-porous Davison silica, we have found it necessary to use an initial equilibration time of 12 h and 2 h for subsequent isotherm points (*1*, *11*). These very long equilibration times may allow H_2 spillover from Ru onto Cu. While H_2 chemisorption on Cu would be expected to be weak, it may not be reversed by the short evacuation time (10 min) used and therefore also appear in the "strong" chemisorption. Experiments to confirm these hypotheses are in progress.

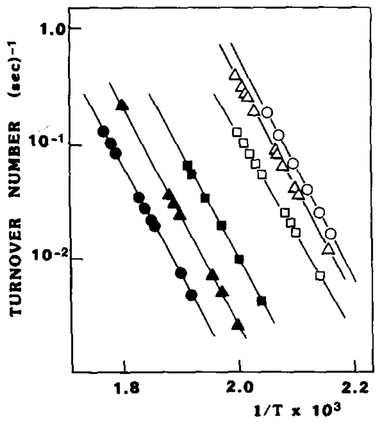

FIG. 1. An Arrhenius plot of turnover number for each of the catalysts listed in Table 1. (A) ○, (A′) ●, (B) △, (B′) ▲, (C) □, (C′) ■.

Even though there is little evidence for Ru–Cu interaction in the H_2 chemisorption, it is obvious in the ethane hydrogenolysis activity changes exhibited in Fig. 1 and the degree of influence of Cu on Ru activity correlates with dispersion in the manner previously observed by Sinfelt *et al.* (*12*). This qualitative correlation between the degree of activity depression (ratio of pure Ru to Ru–Cu catalyst) is shown in Fig. 2 for the three catalysts listed in Table 1 plus the appropriate data for those catalysts from Sinfelt (*2*) and Rouco *et al.* (*1*). Sinfelt *et al.* (*12*) rationalized this correlation by assuming that Cu effectively chemisorbs on the surface of Ru particles so as the dispersion decreases at constant overall Ru:Cu atomic ratio, the surface Ru to total Cu ratio will decrease resulting in a greater fraction of the Ru covered by Cu. To understand the precipitous decrease in ethane hydrogenolysis activity, it was proposed that this reaction requires an ensemble of Ru atoms to constitute a site and that covering only a part of the site with Cu effec-

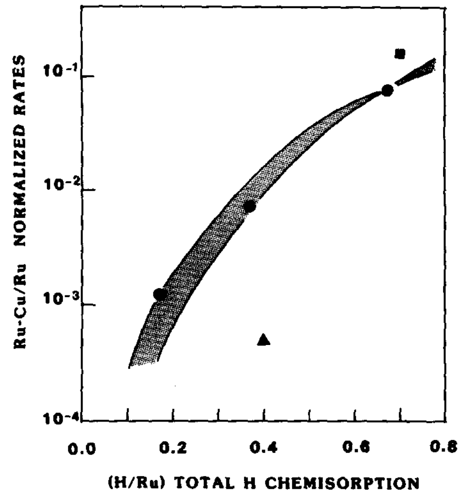

FIG. 2. The rate of ethane hydrogenolysis at 500 K on Ru–Cu/SiO_2 (1 wt% Ru; 1 : 1 Ru : Cu ratio) normalized to 1 wt% Ru/SiO_2. The circles are for the catalysts listed in Table 1; the square is from Ref. (*1*) and the triangle from Ref. (*2*).

tively deactivates it. Assuming an ensemble size of three to four and further assuming that one Cu atom is sufficient to deactivate the whole site one can approximately correlate our data (the shaded area in Fig. 2).

It seems obvious from the correlation given in Fig. 2 that the anion of the impregnating solution and the texture of the support do not directly affect Ru–Cu interaction but do so indirectly by their effect on the dispersion of Ru. The mechanism by which this occurs may be that proposed by Anderson (*13*). Anderson points out that in any impregnation, a certain amount of cation adsorption (ion exchange) occurs and, to the extent that cation adsorption strength differs for the two metals, there will be a certain amount of segregation of the metals as the solution enters the support. This will lower the probability of metal–metal interaction upon reduction. This kind of segregation would be aggravated by the microporous Davison SiO_2 and result in less Ru–Cu interaction as observed. Apparently the nitrate complexes of Ru undergo stronger ion exchange on silica than the chloride-containing complexes and this results in a better dispersion of Ru but the accompanying segregation decreases the likelihood of Ru–Cu interaction. Experiments are in progress which will attempt to demonstrate that this interpretation is the correct quantitatively.

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