JOURNAL OF CATALYSIS 52, 542–543 (1978)

Activation of Nitrogen on Ru–Fe Bimetallic Catalyst

A number of studies have been reported on the catalytic properties of bimetallic catalysts in which it has been pointed out that the surface composition responsible for the catalytic properties is markedly different from the bulk composition (*1*, *2*). In other words the catalytic property of a bimetallic catalyst would indicate the surface composition. Although iron and ruthenium are both effective for the activation of the nitrogen molecule, the rate of ammonia synthesis on iron catalyst increases with the flow rate of synthesis gas (*3*), whereas the rate of synthesis on ruthenium is independent of the flow rate (*4*). In this respect it is interesting to investigate the catalytic properties of Ru–Fe bimetallic catalyst. This report deals with the isotopic equilibration of nitrogen as well as the ammonia synthesis on Ru–Fe as compared with the known results on Fe (*3*, *5–7*) and Ru (*4*, *8*).

A Ru–Fe bimetallic catalyst was prepared by hydrogen reduction of an equimolar mixture of $RuCl_3$ and $FeCl_3$ (both above 99.9%), which was obtained from a mixed aqueous solution by evaporation to dryness. The reduction was carried out at increasing temperatures up to 480°C until no hydrogen consumption was detected: for 5 hr at 200°C, for 10 hr at 370°C, and for 100 hr at 480°C. The surface area of the reduced catalyst was 2.8 m^2/g and did not change after the runs. The X-ray diffraction of the prepared catalyst gave an hcp structure identical to that of ruthenium powder, whereas the lattice constants ($a = 2.641$ Å, $c/a = 1.596$) were smaller in both a and c axes than were those of ruthenium ($a = 2.706$ Å, $c/a = 1.582$), indicating the formation of a Ru–Fe alloy. In fact the lattice constants are in agreement with the values for a Ru–Fe alloy of 60 at.% Ru as reported by E. Raub and W. Plate (*9*).

The experimental procedures for the rate measurements were the same as previously reported (*8*). The isotopic equilibration runs were carried out at 150 Torr of total nitrogen pressure and the ammonia synthesis runs were carried out at 600 Torr of circulating synthesis gas ($H_2/N_2 = 3/1$) with a flow rate of 4.2 liters/hr using 2.6 g of the Ru–Fe catalyst.

The Arrhenius plots for the rates of ammonia synthesis and isotopic equilibration per unit surface area of Ru–Fe are shown in Figs. 1 and 2, respectively, together with the known values on ruthenuim and iron under similar conditions. The apparent activation energies

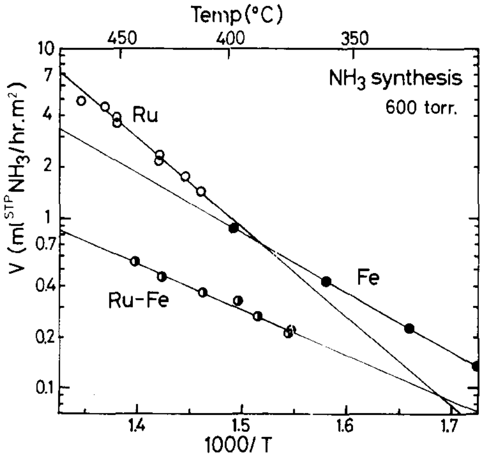

FIG. 1. Arrhenius plots of the rate of ammonia synthesis on Ru–Fe, Ru (*8*), and Fe (*7*) at 600 Torr.

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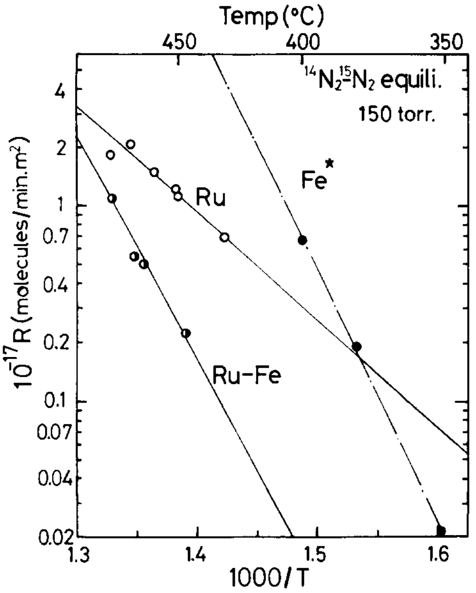

FIG. 2. Arrhenius plots of the rate of isotopic equilibration of nitrogen on Ru–Fe, Ru (*8*), and Fe (*6*) at 150 Torr. The asterisk indicates that the rates on Fe are estimated from known values obtained under 355 Torr assuming one-half-order kinetics found by Schulz and Schaefer (*11*).

(E_a) are obtained from these plots and are given in Table 1. It is clear that the value of E_a on Ru–Fe is close to that on Fe rather than on Ru for both reactions, suggesting that the surface property of the Ru–Fe catalyst is governed by the iron component. In view of this fact, the effect of flow rate on the rate of ammonia synthesis was examined on the Ru–Fe catalyst. It was found that the rate of ammonia synthesis on Ru–Fe increases with increase in the flow rate of synthesis gas as is the case with pure iron (*3*). Thus the above-mentioned results seem to indicate that the surface of the Ru–Fe catalyst is occupied largely by iron atoms.

There is, however, a large difference in specific activity per surface area between the Ru–Fe and Fe catalysts, with the iron surface being more active, as is clear from Figs. 1 and 2. A simple enrichment of iron does not explain the results, while enrichment would be reasonable on the basis of the smaller heat of sublimation of iron. Presumably the surface iron atoms on the Ru–Fe catalyst form less readily the active sites required for the activation of nitrogen as depicted by Boudart and co-workers (*10*) on Fe/MgO catalyst.

TABLE 1

Catalyst	E_a (kcal/mol)	
	Ammonia synthesis	Isotopic equilibration
Ru	24 (*8*)	24 (*8*)
Ru–Fe	13	52
Fe	16 (*7*)	58 (*6*)

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Received October 7, 1977