JOURNAL OF CATALYSIS 54, 436–438 (1978)

NOTES

Isotopic Equilibration of Nitrogen on Potassium-Promoted Transition Metal Catalysts[1]

It has been reported that the addition of potassium to transition metals remarkably enhances the rate of ammonia synthesis (*1*). It has been also revealed that the potassium addition shifts the most active elements from Fe or Os to Ru (*2*). This pattern of activities can be expected for the isotopic equilibration of nitrogen over transition metals, since the ammonia synthesis reaction requires the dissociation of a nitrogen molecule. The catalytic activities of transition metals for the isotopic equilibration of nitrogen are known for Fe (*3*), Ru (*4*), Os (*5*), Co (*6*), Raney Ni (*6*), Re (*7*), W (*8*), and Mo (*9*), while no comparative study of metals has been made.

The potassium-promoted transition metal/carbon catalysts were prepared in the same manner as used previously (*1*). Active carbon (Tsurumi coal, 1000 m^2/g) was impregnated with an aqueous solution of the chloride of each transition metal (nitrate for Fe) and the metal salt was reduced by hydrogen at increasing temperatures up to 400°C (final temperature for Re, 440°C; for Fe, 430°C) for about 50 hr. The content of metal was commonly 5% (w/w) carbon as metal. The added potassium metal was distributed throughout the catalyst bed by circulating helium at around 400°C for 20 hr. The amount of adsorbed potassium was almost in the range of 17 to 20% (w/w) carbon (11% for Ni). The apparatus was a closed circulating system comprising a reactor. The isotopic mixture of nitrogen gas (^{15}N, about 20 atom%) was adsorbed in advance on the catalyst at the reaction temperature until an adsorption equilibrium was established under the reaction pressure (150 Torr) for more than 20 hr. The change in the isotopic composition of circulating gas with time was continuously followed by mass spectrometry. The equilibration rate, R (molecules/min·g), was determined from the first-order plot of $^{29}N_2$ mole fraction.

Although a slow equilibration was observed on Pd–K/C at 400°C, the rate value (1.1×10^{16}) was not much larger than that on K/C (0.3×10^{16}) at 400°C, which can be ascribed to iron impurity in the carbon (about 0.1%). Since no ammonia synthesis activity was detected on Pd–K supported on coconut carbon at 450°C (*2*), the real activity of the Pd catalyst would be very small if any. The observed rates on the other nine metal catalysts are shown in Fig. 1 as Arrhenius plots. It is obvious that Ru is outstandingly active in this catalyst system.

Strictly speaking the activities of metals should be compared on a rates per metal area basis. The chemisorption of hydrogen or carbon monoxide has been utilized to estimate the metal area, whereas, in the present case, the well-known spillover of hydrogen as well as the carbonyl formation

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[1] Activation of Nitrogen by Alkali Metal-Promoted Transition Metal, VII.

0021-9517/78/0543-0436$02.00/0

on base metals renders the result unreliable. In view of the high surface area of the support, however, it may be expected that the extents of dispersion of metal on carbon do not differ too greatly from one another. The difference would be within two- or threefold. Although the metal area data are thus unavailable, the relative rates on metals on a gram of catalyst basis would be sufficient to give an activity pattern which is qualitative in nature.

As is shown in Fig. 1, the reaction temperature ranges were different depending on the activity of catalyst, while the rates at a common temperature of 350°C can be determined from the plots. The values of R at 350°C are given in Fig. 2 as a function of $-\Delta H_0°$ (kilocalories per metal atom), the heat of formation of metal oxides, which has been shown to be a parameter for the heat of chemisorption of gases (*10*). Although a curve is drawn through the highest points, it does not give any particular meaning, since there are large deviations. However this sort of presentation can give a general idea of the activity pattern at a glance. The general trend is, as expected, almost the same as that for the ammonia activity (*2*), while the superiority of Ru over other metals is more pronounced in the equilibration activity.

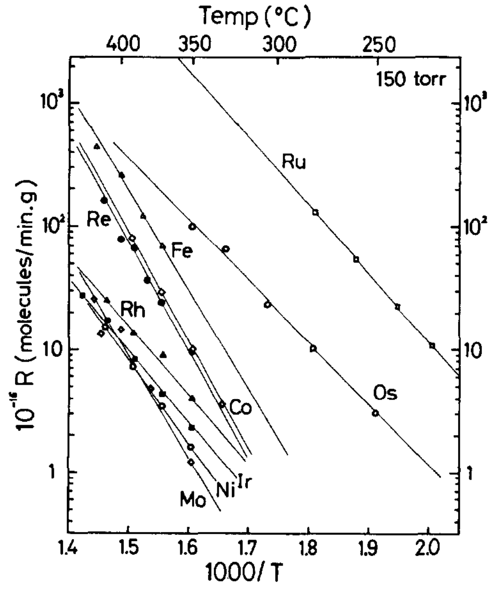

FIG. 1. Arrhenius plots of equilibration rate on transition metal–K/AC catalysts under 150 Torr.

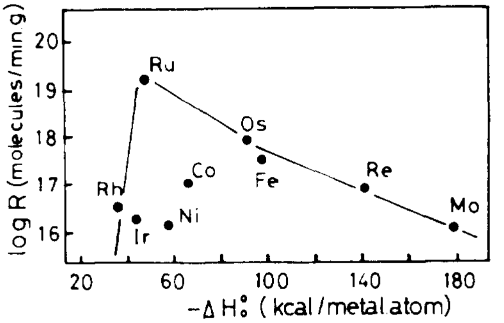

FIG. 2. Equilibration rates at 350°C as a function of $-\Delta H_0°$.

It may be pointed out that there is a definite trend that the iron family of metals (Fe, Ru, and Os) exhibits the maximum activities in each series of metals of the periodic table.

On the basis of the apparent activation energies, estimated from the temperature dependence of equilibration rate, the transition metals can be classified into two groups:

(1) Ru (23), Rh (25), Os (22), Ir (26);
(2) Re (40), Mo (38), Fe (35), Co (38), Ni (31).

The values in parentheses are the apparent activation energies (kilocalories per mole). The group 1 metals are known to be noble and not to form nitrides, while the group 2 metals are known to be less noble and to form nitrides (*11*). The lower activation energies on noble metals may be understood on the basis of their smaller affinity to nitrogen. That is, the smaller affinity should give rise to a limited surface coverage by nitrogen during the equilibration so that the observed activation energy is close to the activation energy for adsorption, while the apparent activation energies on less noble metals are probably closer to the activation energy for desorption because of their greater affinity to nitrogen. It is natural that the activation energy for desorption is larger than that for adsorption. Indeed no such tendency is found for the ammonia synthesis (*1*), the rate of which is probably determined by the chemisorption of nitrogen over metals.

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Received October 7, 1977; revised April 16, 1978