for this is seemingly the high activation energy for adsorption and the low heat of adsorption. Weinberg and co-workers also estimated the activation energy for adsorption of molecular nitrogen to be 67 kJ/mol at $\theta_N = 0$ and the heat of its adsorption as 25 kJ/mol at their reaction temperatures.[30] They also estimated the activation energy for desorption of nitrogen from the platinum (110)-(1×2) surface as 108–117 kJ/mol, which is independent of nitrogen coverage.

Conclusion

The rate of catalytic decomposition of ammonia is often markedly retarded by hydrogen, as given by eq 8. Under these conditions the reaction is successfully explained by the well-known Temkin–Pyzhev mechanism, which assumes that the desorption rate of chemisorbed nitrogen is rate determining.

The kinetic equation of the reaction on tungsten, on the other hand, is expressed by eq 1 and may well be independently explained by the Langmuir–Hinshelwood mechanism, which assumes that the rate is proportional to the amount of ammonia molecules adsorbed on the catalyst surface. However, examination of the behavior of nitrogen chemisorbed directly under the reaction conditions reveals that the mechanism of the reaction is not accurately described by the Langmuir–Hinshelwood mechanism, but rather by a dynamic balance between the supply and desorption of chemisorbed nitrogen.

It has now been demonstrated for the first time that the two mechanisms are the limiting cases of a "new" general mechanism. If the chemisorbed nitrogen that is supplied from ammonia is readily hydrogenated to re-form ammonia before it is desorbed to form nitrogen molecules, then the quasi-equilibrium of eq 9 is realized in the steady state of the reaction. In this case the reaction proceeds via the Tempkin–Pyzhev mechanism and shows a marked retardation by hydrogen. On the other hand, if the chemisorbed nitrogen is mostly desorbed before it is hydrogenated, then the tungsten-type behavior should be observed, for which there is no retardation by hydrogen. Accordingly, the kinetics of ammonia decomposition on metals is determined by whichever of the two rates, hydrogenation and desorption of chemisorbed nitrogen, would be faster. If the former is much faster than the latter (which is the case, in general, at lower temperatures and higher hydrogen pressures), then the Temkin–Pyzhev mechanism occurs, whereas if the latter is much faster than the former (which is the case, in general, at higher temperatures and lower hydrogen pressures) the tungsten-type behavior is observed. In such a manner, ammonia decomposition on metals generally proceeds between the two limiting cases. The activation energy for adsorption and the heat of adsorption of nitrogen on platinum can be estimated on the basis of the general mechanism.

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Additions and Corrections

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Josef Michl* and Erik W. Thulstrup: Ultraviolet and Infrared Linear Dichroism: Polarized Light as a Probe of Molecular and Electronic Structure.

On p 198, the twist angle in 4,4′-dibromobiphenyl derived from IR dichroic measurements is incorrectly stated to be 30–40°. The correct value is 60–85°.