JOURNAL OF CATALYSIS **114**, 457–459 (1988)

NOTES

On the Structure Sensitivity of Ammonia Synthesis on Promoted and Unpromoted Iron

In recent years the techniques of surface science have been applied to the elucidation of the details of the mechanism of ammonia synthesis on Fe. In particular Ertl and co-workers (*1–7*) have demonstrated the strongly anisotropic nature of nitrogen adsorption on well-defined Fe single-crystal surfaces. Thus, as shown in Table 1, the (111) plane is by far the most active for such dissociation, a property thought to be due to the presence of exposed seven-coordinated Fe atoms in this surface (*8*). The trend in the efficiency of nitrogen dissociation on these planes has been shown by Spencer *et al.* (*9*) to parallel their activity for ammonia synthesis under kinetically limited conditions; thus the (111) plane shows 400 times the activity of the relatively smooth (110) surface.

Ertl *et al.* (*1, 4, 7*) have also investigated the effects of the presence of alkali metal on the nitrogen adsorption kinetics and have found that the main effect on the energetics is an increase in the heat of adsorption of molecular nitrogen, and a consequent reduction in the energy barrier to dissociation at the surfaces. They then postulate that the effect of promotion in industrial ammonia synthesis is to bring all planes to a similar activity (*1b*), with the (111) plane being least affected and the (110) being most affected. The purpose of the present Note is to present data from the kinetic modeling of ammonia synthesis using the data derived by Ertl *et al.* and to examine whether the thesis described above regarding promoter action is correct.

The program for calculating ammonia synthesis rates has been described in some detail previously (*10*). In the present case the reaction is simulated in a plug flow reactor of volume 1 cm^3 and flow rates can be varied from very low levels (10^{-10} cm^3 s^{-1}), which produce equilibrium yields (~16% (*11*)) of ammonia under the present condition (720 K, 107 atm pressure), to those approximating test conditions in microreactors (*12*) (~0.05 cm^3 s^{-1}), to high flow rates to test the catalytic kinetics (50 cm^3 s^{-1}). The surface area of the catalyst is assumed to be 5 m^2 g^{-1}, similar to published values for such catalysts (*11*). Within the model, then, the kinetics appropriate to the three major index faces, with and without the presence of alkali, have been put into the program; these kinetics are listed in Table 2 and are taken from the publications of Ertl *et al.* (*1–7*). In Table 2 the units of E are kilojoules per mole and A is in molecules per cubic centimeter per second, the derivation of the latter having been described in our earlier publication (*10*). The ammonia yields obtained from our modeling are shown in Table 1, for the two higher flow rates mentioned above.

It is noted that yields from the input kinetics are lower than those seen in practice and the reasons for this have been discussed elsewhere (*10, 13*). In the present paper we are concerned with the effect of promotion and morphology on synthesis rate. The yields of ammonia at 0.05 cm^3 s^{-1} flow rate do not support the Ertl *et al.* postulate. The yields, however, are in the ratio 5:2.1:1 for promoted Fe(111):(100):(110), respectively, relative to the (110) plane. This compares with yield ratios for unpromoted Fe of 31:2.5:1 from this work, 420:25:1 from the experiment of Spencer *et al.* (*9*), and the dissociation rate ratio of 60:3:1 from the data of Bozso *et al.* (*2*). It is important to note that although

0021-9517/88 $3.00

TABLE 1

Kinetic Parameters for Nitrogen Dissociation and Ammonia Synthesis on Fe Single-Crystal Planes

Plane	Nitrogen dissociation rate (relative to clean Fe(110))[a]	Ammonia synthesis yield (relative to clean Fe(110))		
		Experiment[b]	Modeling[c]	
			Normal flow	High flow
Fe(111)	60	420	32	240
+K	~500 (Ref. (*7*))	—	67	1152
Fe(100)	3	25	2.5	4
+K	~500 (Ref. (*7*))	—	30	413
Fe(110)	1	1	1	1[d]
+K	—	—	14	28

[a] From the publications of Ertl *et al.* (*1–7*).

[b] From Ref. (*9*).

[c] This work. Normal flow is 0.05 $cm^3 s^{-1}$ and high flow is 50 $cm^3 s^{-1}$ both at 107 atm pressure, 720 K.

[d] The absolute yield here is 4.6×10^{-5} mole% ammonia at the exit from the reactor and is 10^{-3} of the yield at normal flow since in both these cases the reaction is in the kinetically limited regime, well away from equilibrium.

the yields from the model at normal flow rates are closer for the three promoted planes than for the unpromoted ones, this result is a little misleading. This is because at the yields considered, the conversion is such that the back reaction is now playing a significant role in the process, so that a doubling of the inherent synthesis rate (forward reaction) does not produce a similar increase in yield. Thus the data at higher flow rates (and hence lower conversion) are more revealing. Table 1 shows that under these conditions the ratio of activity is 240 : 4 : 1 for the unpromoted case and 41 : 15 : 1 for the promoted case (or 10 : 4 : 1 for the latter case if a net dissociation barrier of zero is assumed for the (110) plane).

Thus it seems that, even in the presence of promoter atoms, there is still a marked anisotropy in the ammonia synthesis activity of iron single-crystal planes, when using the data described for these systems in the literature. The surface morphology of industrial ammonia synthesis catalysts is still uncertain and the recently published work of Strongin *et al.* (*15*) shows that even on single crystals, the system is very complex

TABLE 2

Modeled Kinetic Parameters for Ammonia Synthesis on Fe (Units of A are molecules $cm^{-3} s^{-1}$; units of E are kJ $mole^{-1}$)

Plane	Nitrogen adsorption $N_2(g) + Fe \rightarrow N_2$ (a)				Nitrogen dissociation $N_2(g) + Fe \rightarrow N_2$ (a)				References
	Forward		Backward		Forward		Backward		
	$\log_{10}A$	E	$\log_{10}A$	E	$\log_{10}A$	E	$\log_{10}A$	E	
Fe(111)	11.2	0	10.2	31.4	15.2	28.0	21.2	210.0	(*6*)
+K	11.2[a]	0	10.2	46.0	15.2	31.4	21.2	198.7	(*6, 7*)
Fe(100)	11.2	0	10.2	31.4	15.2	52.3	21.2	242.7	(*2a*)
+K	11.2	0	10.2	46.0	15.2	37.7	21.2	213.4[b]	(*2a, 7*)
Fe(110)	11.2	0	10.2	31.4	15.2	60.7	21.2	234.3	(*2b*)
+K	11.2	0	10.2	46.0	15.2	54.4	21.2	217.6	[c]

[a] Ertl *et al.* state that promotion may enhance the sticking probability into the precursor state for dissociation by a factor of 6. Simulation of this effect by increasing $\log_{10}A$ to 11.8 has only a minor effect on yield, increasing it from 2.96 to 3.13%.

[b] There is a little discrepancy in the quoted values for this parameter. This value was taken from Ref. (*7*), whereas Refs. (*1a, 1b, 4*) appear to indicate a value of more like 221.8 kJ $mole^{-1}$. Use of the latter in the model results in yields decreased from 1.3 to 0.9%.

[c] No kinetic study has been published for the effect of promotion on Fe(110) so a similar promoter-induced reduction in E^* (the net activation barrier to dissociation from the gas phase) as determined for Fe(100) has been assumed. If instead E^* is assumed to be zero with the recombination activation energy the same, then the yield at high flow is increased by nearly a factor of 4.

under synthesis conditions. In particular, they find that neither potassium atoms nor oxidized potassium is stable during high-pressure reaction (*14*), while complete surface restructuring appears to take place when alumina is present (*15*). It is possible that in the presence of double-promotion, restructuring to (111) type planes and activation take place (*14*).

It must be noted that the kinetic data described above for Fe crystals were those pertaining to nitrogen dissociation at low coverages. In all the cases modeled above, and as described by ourselves (*10, 13*) and others (*16*) earlier, the coverage of the surface by adsorbate is very high (in the case of unpromoted Fe(111) at 0.05 $cm^3 s^{-1}$ reactant flow rate the nitrogen adatom coverage was 75% of saturation). Thus it would be more reasonable to use higher coverage values for nitrogen dissociation kinetics. The indications are that when such parameters are used (mainly involving a considerably decreased heat of dissociative adsorption for nitrogen) yields similar to those found in high-pressure tests are obtained (*10*). However, the details of the kinetics of the interaction of nitrogen with Fe at high coverages, and particularly in the presence of adsorbed promoter, are poorly understood. The data already obtained for this system have proved invaluable as a basis for discussion of the nature of nitrogen adsorption on these surfaces, but in order to model this reaction successfully and in a consistent manner, further efforts are required to define the entropy changes and the energetics in the high coverage limit and in the presence of promoter.

In conclusion, then, it must be emphasized that the effect of potassium promotion on Fe surfaces of different morphology is to increase the activity of all planes, but *it does not produce surfaces of equal activity*. The synthesis rate ratio between the most active and the most inactive planes decreases from ~240 to ~40 with promotion, but the latter still represents a significant activity difference such that synthesis on (111) planes would dominate if such kinetics were applicable to the commercial industrial process.

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Received June 19, 1987; revised October 7, 1987