Methylamine hydrogenolysis on a rhodium catalyst: kinetics at high hydrogen partial pressures

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The kinetics of hydrogenolysis of methylamine to methane and ammonia on a rhodium catalyst were investigated at hydrogen partial pressures in the range of 2–10 atm at temperatures of 368, 383, and 408 K. At a fixed methylamine partial pressure, the rate decreased with increasing hydrogen partial pressure. When the hydrogen pressure was held constant, the rate increased with increasing methylamine pressure. Results of a previous investigation by our group at lower hydrogen partial pressures (0.01–1 atm) indicated that the hydrogenolysis rate passed through a maximum with increasing hydrogen pressure. Moreover, at the lower hydrogen pressures, there was an inverse rather than positive dependence of the rate on methylamine partial pressure. With the aid of the present results, there is a much clearer definition of the maximum in the experimental data relating the reaction rate to hydrogen partial pressure. The inversion of the effect of methylamine pressure on the rate as the hydrogen pressure is varied over a sufficiently wide range is also firmly established. With regard to the interpretation of the many interesting features of the kinetics, we retain the suggestion from our earlier work that the rate limiting step at the highest hydrogen pressures is the scission of the carbon–nitrogen bond in a partially dehydrogenated methylamine intermediate chemisorbed on the rhodium, with no direct participation of hydrogen as a reactant in this step. At the lowest hydrogen pressures, however, there is a different rate limiting step in which hydrogen does participate directly as a reactant.

Keywords: methylamine hydrogenolysis: (i) kinetics of; (ii) catalysis of, by rhodium; (iii) mechanism of; (iv) effect of hydrogen pressure on; (v) effect of methylamine pressure on

Various metal surfaces catalyze the hydrogenolysis of methylamine to methane and ammonia [1–4]:

$$CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3 \qquad (1)$$

Rhodium is a particularly active catalyst for the reaction [3].

Results of a study of the kinetics of the reaction on a catalyst consisting of small clusters of rhodium dispersed on silica have been reported by our group [4]. Kinetic data at a fixed methylamine partial pressure in the temperature range 353–408 K exhibited a characteristic pattern in which the reaction rate passed through a maximum as the hydrogen partial pressure was increased by two orders of magnitude from 0.01 to 1 atm. At a given temperature, the position of the maximum shifted slightly in the direction of higher hydrogen pressure when the methylamine pressure was increased by one to two orders of magnitude within the range of 0.0014–0.085 atm. Over a broad range of hydrogen partial pressures covered in the investigation, the reaction rate decreased with increasing methylamine pressure. As the hydrogen pressure increased, the inverse dependence of the rate on methylamine pressure became less pronounced and eventually disappeared at a sufficiently high hydrogen pressure. At hydrogen partial pressures somewhat higher than those at which rate maxima were observed, there was an indication that the rate exhibited a positive dependence on methylamine pressure. Thus, there appeared to be an inversion of the directional effect of methylamine pressure on the rate when the hydrogen partial pressure was varied over a sufficiently wide range. However, this interesting feature in the kinetics was not established very well. Rate data at hydrogen partial pressures substantially higher than one atmosphere were clearly desirable for this purpose.

Since additional kinetic data at higher hydrogen pressures would also serve to provide a better definition of the maxima in plots of rate vs. hydrogen pressure, it was decided to extend the investigation to pressures in the range of 2–10 atm. To accomplish this, the flow reactor system described in our earlier paper [4] was modified by inclusion of a back-pressure regulator downstream of the reactor. A stream consisting of a custom mixture of 3 mol% methylamine in hydrogen was mixed with separate streams of hydrogen and helium in appropriate amounts to achieve the desired partial pressures of reactants.

Rate data were obtained at temperatures of 368, 383, and 408 K at hydrogen partial pressures of 2–10 atm and methylamine partial pressures of 0.010–0.070 atm. Rates of formation r of methane, in molecules per second per surface rhodium atom, are given in table 1, along with data for hydrogen partial pressures of 1 atm and lower from our previous paper [4]. The data are also presented in fig. 1 in the form of curves showing the depen-

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Table 1
Rate data for methylamine hydrogenolysis on a rhodium catalyst [a]

T	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$
353	0.0014	0.010	15	0.0040	0.010	12	0.011	0.010	7						
		0.025	32		0.025	26		0.025	16						
		0.050	36		0.050	33		0.050	20						
		0.10	40		0.10	36		0.10	22						
		0.20	36		0.20	36		0.20	24						
		0.50	23		0.50	27		0.50	20						
		0.70	–		0.70	22		0.70	17						
		1.00	16		1.00	18		0.99	14						
368	0.0018	0.010	43	0.0040	0.010	31	0.012	0.010	26	0.032	0.010	17	0.070	–	–
		0.025	120		0.025	93		0.025	72		0.025	51		–	–
		0.050	160		0.050	130		0.050	120		0.050	92		–	–
		0.10	180		0.10	150		0.10	140		0.10	120		–	–
		0.20	180		0.20	160		0.20	150		0.20	130		–	–
		0.50	120		0.50	120		0.50	140		0.50	130		–	–
		0.70	93		0.70	100		0.70	120		0.70	110		–	–
		1.00	69		1.00	87		0.99	97		0.97	94		–	–
								2.0	34		2.0	50		2.0	64
								5.0	10		5.0	16		5.0	22
								7.5	5		7.5	9		7.5	13
								10.0	3		10.0	6		9.9	8
383	0.0018	0.005	60	0.0042	–	–	0.012	0.005	14	0.029	–	–	0.072	–	–
		0.010	140		0.010	80		0.010	44		0.010	22		0.010	–
		0.025	400		0.025	240		0.025	130		0.025	80		0.025	–
		0.050	640		0.050	420		0.050	270		0.050	180		0.050	100
		0.10	730		0.10	530		0.10	390		0.10	300		0.10	220
		0.20	730		0.20	580		0.20	430		0.20	360		0.20	310
		0.50	510		0.50	480		0.50	390		0.50	340		0.50	320
		0.70	390		0.70	390		0.70	340		0.70	310		0.70	310
		1.00	270		1.00	300		0.99	260		0.97	270		0.93	260
								2.0	180		2.0	220		2.0	260
								5.0	63		5.0	84		5.0	110
								7.5	36		7.5	50		7.5	66
								10.0	28		10.0	40		9.9	52

Table 1 (Continued)

T	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$	p_M	p_H	$10^5 \times r$
393	0.0016	0.011	220	0.0040	0.010	100	0.012	0.010	45	0.028	0.010	21	0.077	0.010	7
		0.025	620		0.025	360		0.025	190		0.025	100		0.025	41
		0.062	1200		0.050	780		0.050	480		0.050	280		0.050	130
		0.12	1300		0.10	1100		0.10	830		0.10	610		0.10	350
		0.20	–		0.20	1300		0.20	1000		0.20	820		0.20	610
		0.50	1100		0.50	1100		0.50	940		0.50	860		0.50	670
		0.70	930		0.70	970		0.70	810		0.70	810		0.70	620
		1.00	680		1.00	760		0.99	650		0.97	700		0.92	570
408	0.011	0.010	56	0.032	0.010	27	0.085	0.010	17						
		0.025	320		0.025	190		0.025	97						
		0.050	1000		0.050	640		0.050	320						
		0.10	2200		0.10	1600		0.10	990						
		0.20	3100		0.20	2900		0.20	2100						
		0.50	3100		0.50	3200		0.50	2800						
		0.70	2800		0.70	3000		0.70	2700						
		0.99	2000		0.97	2500		0.92	2700						
		2.0	1400		2.0	1800		2.0	2200						
		5.0	600		5.0	830		5.0	1200						
		7.5	370		7.5	530		7.5	820						
		10.0	260		10.0	380		9.9	620						

[a] Column headings: T, temperature (K); p_M, methylamine partial pressure (atm); p_H, hydrogen partial pressure (atm); r, reaction rate (s^{-1}). Data at hydrogen partial pressures $\leqslant 1$ atm taken from ref. [4].

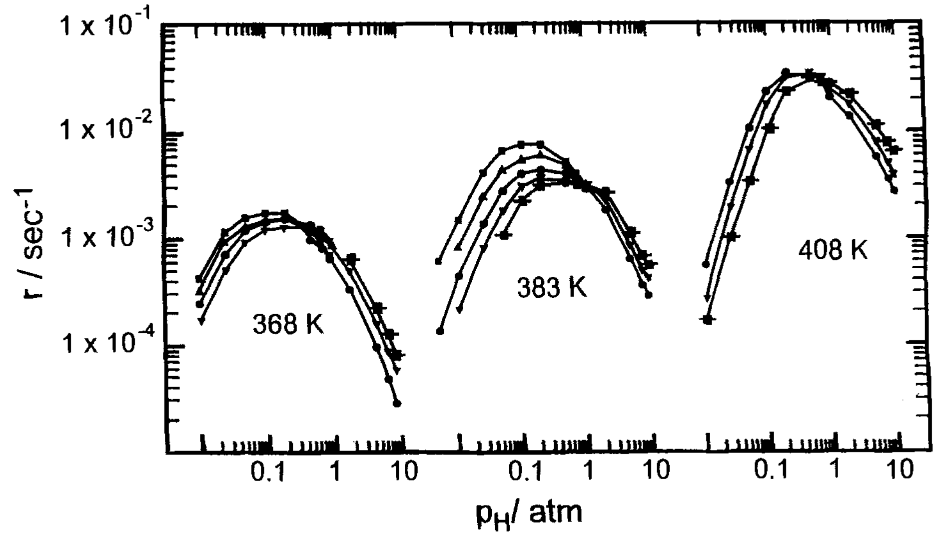

Fig. 1. Rate of hydrogenolysis of methylamine to methane and ammonia on a rhodium catalyst as a function of hydrogen partial pressure p_H for a series of different partial pressures of methylamine at temperatures of 368, 383 and 408 K. The catalyst consisted of small rhodium clusters dispersed on silica with a rhodium content of 1 wt% and a metal dispersion (ratio of surface Rh atoms to total Rh atoms) of 1. The rate r is given in molecules per second per surface rhodium atom (units shown simply as s^{-1} in the ordinate). Each of the different symbols used for data points represents data at a given level of methylamine partial pressure: (■) 0.0018 atm; (▲) 0.0040–0.0042 atm; (●) 0.011–0.012 atm; (▼) 0.029–0.032 atm; (╋) 0.070–0.085 atm. The rate data for hydrogen partial pressures of 1 atm and lower were taken from ref. [4].

dence of the rate on hydrogen partial pressure p_H at a constant methylamine partial pressure, for a series of different values of the latter. Data taken from our previous paper for temperatures of 353 and 393 K and hydrogen pressures of 1 atm and lower are shown in fig. 2 to complete the presentation of the kinetic data.

At hydrogen partial pressures in the range of 2–10 atm, the rate of hydrogenolysis of methylamine clearly increases with increasing methylamine pressure. This contrasts with the inverse dependence on methylamine pressure observed at hydrogen partial pressures substantially lower than about 1 atm. Although there was an indication of this feature in the kinetics in our earlier investigation [4], the present results establish it much more firmly. The new data also improve the definition of the functional relationship between reaction rate and hydrogen pressure. In particular, the rate maxima are now defined more clearly over the whole range of temperatures investigated, and the effect of methylamine pressure on the rate is known in some detail on both sides of the maxima.

Mechanistically, the hydrogenolysis of methylamine on various metals is believed to proceed through a partially dehydrogenated methylamine intermediate chemisorbed on the surface [1,2,4]. Scission of the carbon–nitrogen bond in this species is followed by hydrogenation of the resulting carbon-containing and nitrogen-containing fragments to yield methane and ammonia.

The complexity of the kinetics found in our studies on rhodium have led us to conclude that the rate limiting step of the reaction changes over the wide range of hydrogen partial pressures covered in the investigation [4]. As stated in our earlier paper [4], kinetic schemes based on a single rate limiting step for the whole range of variables investigated do not provide an adequate quantitative description of the main features of the data, or they are questionable from a mechanistic standpoint.

At the highest hydrogen pressures employed in our studies, where the rate varies inversely with hydrogen pressure and exhibits a positive dependence on methylamine pressure, we believe that the rate limiting step is one in which scission of the carbon–nitrogen bond

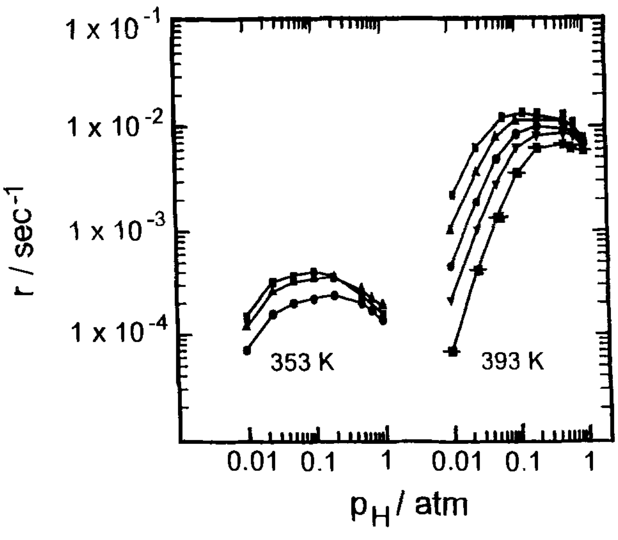

Fig. 2. Data on rate of methylamine hydrogenolysis as a function of hydrogen pressure p_H at temperatures of 353 and 393 K for the same rhodium catalyst for which rate data are given in fig. 1. Methylamine partial pressures are: (■) 0.0014–0.0016 atm; (▲) 0.0040 atm; (●) 0.011–0.012 atm; (▼) 0.028 atm; (╋) 0.077 atm. The data are taken from ref. [4].

occurs in the partially dehydrogenated methylamine intermediate mentioned earlier. Hydrogen does not participate directly as a reactant in this step. However, at the lowest hydrogen pressures, where the rate exhibits a positive dependence on hydrogen pressure and an inverse dependence on methylamine pressure, we suggest that the rate limiting step is one in which there is participation of chemisorbed hydrogen as a reactant [4]. For example, the reaction of chemisorbed hydrogen with carbon-containing and nitrogen-containing fragments formed in the scission of the carbon–nitrogen bond could be rate limiting.

As stated in our earlier paper [4], we have not made a kinetic treatment of a sequence of steps which is complete enough to provide a sufficiently general rate equation allowing for changes in rate limiting steps. For such a treatment to be really meaningful, additional information on kinetic parameters of possible elementary steps would be helpful, either from direct kinetic measurements or from estimates using thermochemical information for the steps. The very extensive set of kinetic data now available for methylamine hydrogenolysis on rhodium make it an excellent candidate for a "microkinetic" analysis [5].

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