

TRANSITION METAL CATALYSIS OF THE HETEROGENEOUS DECOMPOSITION OF HYDRAZINE: ADIABATIC KINETICS BY ACCELERATING RATE CALORIMETRY

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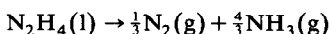
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ABSTRACT

The thermochemical kinetics of the transition-metal-catalyzed decomposition reaction of hydrazine have been studied using accelerating rate calorimetry. The reaction stoichiometry was determined by both product analysis and thermochemical balance. In the range 350–515 K when both liquid and vapor hydrazine are present, the decomposition proceeds according to:



with $\Delta H_{\text{rxn}} = -123.3 \text{ kJ mol}^{-1}$ (515 K). In the range 515–590 K when only vapor is present in the reaction system, $\Delta H_{\text{rxn}} = -154.8 \text{ kJ mol}^{-1}$ (515 K).

The reaction shows apparent zero-order kinetics and the rates were found to be proportional to the surface area of added metals in the form of powders or foils. Rates and activation parameters are reported for ten transition metals and the Fe:Ni:Cr alloy, 304L stainless steel.

The activation energies and relative specific activities at 353 K are: Co (43 kJ mol⁻¹, 3900); Ni (93 kJ mol⁻¹, 310); Mo (76 kJ mol⁻¹, 94); V (85 kJ mol⁻¹, 66); Fe (119 kJ mol⁻¹, 33); W (68 kJ mol⁻¹, 11); Au (74 kJ mol⁻¹, 7.8); Ti (95 kJ mol⁻¹, 1.0); 304L (100 kJ mol⁻¹, 0.43); Cr (105 kJ mol⁻¹, 0.099); Ta (106 kJ mol⁻¹, 0.06).

The Arrhenius activation parameters for the various metals (and different samples of the same metal) show a linear compensation effect: $\ln A = (1/\theta)E_a/R + \ln k_0$, with a compensation temperature, θ , of 445 K. Different samples of molybdenum powders showed $\theta = 432 \text{ K}$ and an isokinetic temperature of 430 K, at which the rates for all molybdenum samples were equal.

The relative activities are explained in terms of the binding energies of N-adatoms to the metal surface and an empirical thermochemical relationship is proposed. Additionally it is noted that the least catalytically reactive metals are those whose ambient-atmosphere oxide films are not reduced by hydrazine.

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This work presents a new and useful application of the ARC technique to the study of heterogeneous catalysis and may find particular importance in the selection of materials and choice of design parameters to minimize thermal hazard problems in hydrazine systems.

INTRODUCTION

The surface-catalyzed decomposition reaction of hydrazine is of great importance in aerospace applications [1]. An alumina-supported iridium catalyst [2] is used in satellite thruster systems and for emergency power generation in advanced aircraft [3]. This rapid, exothermic and gas-producing decomposition, while useful under propulsion conditions, presents significant problems in the selection of materials for hydrazine storage and handling systems [4].

The variety of techniques which have been applied to the study of the hydrazine decomposition reaction include surface spectroscopies [5], adsorption/desorption [6], flow reactor [7] and isothermal kinetic studies [8]. In our earlier work we demonstrated that accelerating rate calorimetry was an attractive approach to the study of the adiabatic kinetics of hydrazine decomposition [9]. The accelerating rate calorimeter (ARC) allows the measurement of rates and activation parameters for an exothermic reaction over a wide range of temperatures [10–12]. Analysis of the ARC temperature and pressure rates as a function of temperature allows the determination of the basic rate parameters [9].

Kinetic and mechanistic conclusions based on studies of the hydrazine decomposition reaction could be of significance in unraveling the complex biological [13] and industrial [14] processes for the fixation of dinitrogen. Many of the same intermediates are proposed for all three processes.

In this paper we present the results of a study of the non-isothermal kinetics of the heterogeneous decomposition of hydrazine catalyzed by polycrystalline transition metal powders and foils.

EXPERIMENTAL

Hydrazine was monopropellant grade (MIL-P-26536D) which had been carefully stored to minimize exposure to atmospheric carbon dioxide and moisture. These contaminants have been found to cause irreproducible results in ARC experiments. The typical carbon dioxide content of the hydrazine was less than 20 ppm. Metal powders and foils were obtained commercially (Aesar Group, Seabrook, NH, or Alpha Corp., Danvers, MA) and were greater than 99.8% pure. Metal powders were of a narrow size distributions ($3\text{--}7\text{ }\mu\text{m}$) or sieved to $-200/+325$. Foils and turnings were degreased with isopropyl alcohol and dried under nitrogen. Pre-treatment of

the metal samples consisted of stirring the materials overnight in hydrazine under a nitrogen atmosphere. Adsorbed hydrazine was removed by heating to 343 K under vacuum. Surface areas of powders and turnings materials were measured using a Micromeritics Flowsorb II Model 2300 surface area analyzer with nitrogen or krypton as the adsorbent gas (Brunauer–Emmett–Teller (BET) areas). Surface areas of foils were geometric areas.

The ARC instrument (Columbia Scientific Industries, Austin, TX) has been described elsewhere [10]. The instrumental protocol, experimental procedures, analytical methods and data analysis technique have been detailed earlier [9,11,12]. For these experiments, 9 ml titanium reaction vessels were charged with 0.5 ml of hydrazine and 0.01–1.5 g of metal powder, foil or turnings under a nitrogen atmosphere. The decomposition reactions were carried out in sealed reaction vessels without the attachment of a pressure transducer or other connections to the outside of the calorimeter. Each experiment was performed with a new reaction vessel and a different sample of catalyst.

RESULTS

The hydrazine decomposition reaction [9] takes place according to:



Since the surface of the titanium reaction vessel itself is capable of catalyzing the decomposition of hydrazine, a number of runs were conducted to determine a “background” rate for the adiabatic decomposition of hydrazine in a titanium vessel [4]. For a 30 g reaction vessel with a 0.5 g charge of hydrazine, the onset of the minimum detectable temperature rate of 0.02 K min^{-1} was noted at $468 \pm 5 \text{ K}$. A temperature-rate step, indicating the disappearance of liquid hydrazine (only vapor hydrazine remains) was noted at about half-reaction ($515 \pm 5 \text{ K}$). The final temperature was $585 \pm 5 \text{ K}$. A detailed discussion of these features has been given in an earlier paper [9]. It should be noted that the temperatures quoted here are system dependent and reaction set-ups with different thermal dilution factors could show different start and end temperatures. Figure 1 shows a comparison of a background reaction and a reaction to which 19.3 mg (46 cm^2) of 3–7 μm molybdenum powder had been added. The onset for the molybdenum-catalyzed reaction occurs at 390 K and the step is barely noticeable as a perturbation near the rate maximum at 455 K. The slope of the log (temperature rate) vs. $1/T$ plot for the molybdenum-catalyzed reaction indicates an activation energy of 71.7 kJ mol^{-1} . The activation energy of the background decomposition shown in Fig. 1 is 97.3 kJ mol^{-1} .

In a series of experiments with increasing surface areas of 304L stainless steel powders, a proportional lowering of the onset temperatures was ob-

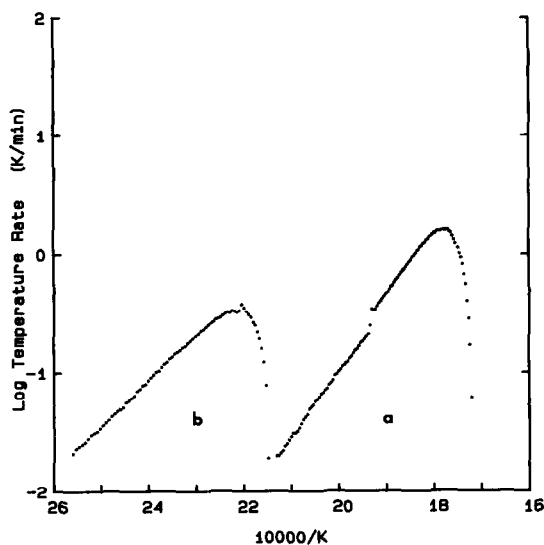


Fig. 1. Hydrazine decomposition reaction kinetics in the ARC for background run in titanium vessel (plot a) and with 46 cm² of added molybdenum powder (plot b). The approximately 30 g titanium reaction vessel contained about 0.5 g hydrazine in both cases.

served (Fig. 2). The reaction rate at a given temperature was found to be proportional to the surface area of the added powders. The activation energies for this series of 304 L SS-catalyzed decompositions (96–103 kJ mol⁻¹) are similar to that observed in the titanium vessel itself.

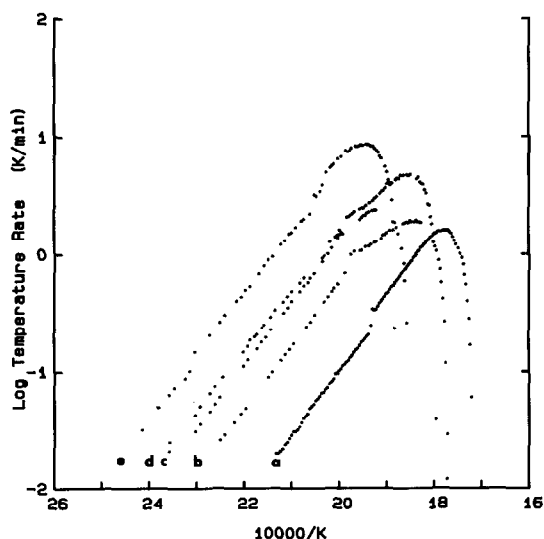


Fig. 2. Hydrazine decomposition kinetics in the ARC for background run in titanium vessel (plot a) and with 119 cm² (plot b), 312 cm² (plot c) and 626 cm² and 1284 cm² of added 304L stainless steel powders (plot d). The approximately 30 g titanium reaction vessel contained about 0.5 g hydrazine in all cases.

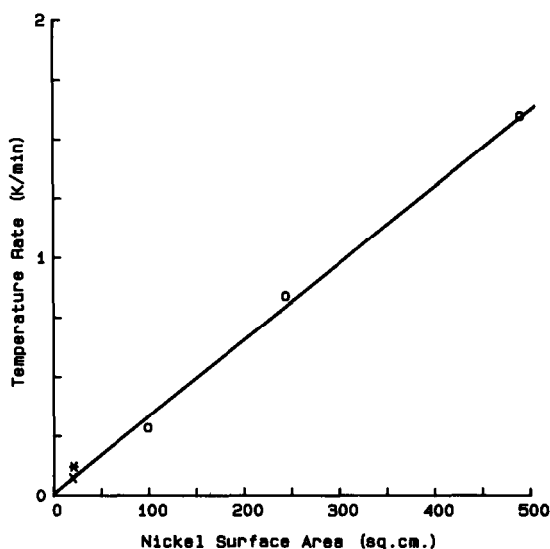


Fig. 3. Hydrazine decomposition rate as a function of surface area of added nickel powders (○), foil (*) and turnings (×). The approximately 30 g titanium reaction vessel contained about 0.5 g hydrazine in all cases.

The rates of decomposition of hydrazine at 393 K, catalyzed by nickel in the form of powders, foils, and machine turnings, were proportional to the surface areas of nickel added (Fig. 3) and independent of the form of the nickel catalyst.

For hydrazine decomposition at temperatures up to 585 K, both thermochemical and chemical analysis of the reaction products of background runs and runs with catalytic material (iron powder) present were consistent with the stoichiometry and heats shown below: eqns. 2, 3.



$$\Delta H = -123.3 \text{ kJ mol}^{-1} \text{ (515 K)}$$



$$\Delta H = -154.8 \text{ kJ mol}^{-1} \text{ (515 K)}$$

This stoichiometry is typical of the low temperature decomposition of hydrazine and has been observed by others in the presence of a wide variety of surfaces [4,15]. A trace of hydrogen was detected in the products.

Based on this stoichiometry, the observed temperature rate (K min^{-1}) was converted to a reaction rate ($\text{mol m}^{-2} \text{ s}^{-1}$) using the system heat capacity, enthalpy of reaction and surface area of catalyst. The catalytic reaction rate was then corrected for the background rate due to the titanium vessel. Arrhenius activation parameters were determined for the pre-step portion of the reaction using an assumed zero-order rate law. The tempera-

TABLE 1

Activation parameters for the transition-metal-catalyzed decomposition of hydrazine

Metal	A^a ($\text{mol m}^{-2} \text{ s}^{-1}$)	E_a (kJ mol^{-1})	Relative reactivity b
Ti ^c	1.15×10^6	92.2	
	1.55×10^6	95.4	
	9.76×10^5	97.3	
	1.61×10^6	97.4	
av. ^d	1.1×10^6	95	1.0
V	4.17×10^4	77.9	
	1.73×10^6	82.3	
	8.03×10^6	86.5	
	1.64×10^6	89.4	
av. ^d	2.4×10^6	85	66
Cr	1.40×10^6	99.7	
	3.04×10^6	105.3	
	4.46×10^6	107.1	
	7.38×10^7	119.9	
av. ^d	3.3×10^6	105	0.099
Fe	4.51×10^8	100.5	
	6.29×10^{11}	123.3	
av. ^d	1.3×10^{11}	119	33
Co	6.97	36.3	
	2.51×10^2	45.3	
av. ^d	8.6×10	43	3900
Ni	2.85×10^5	71.3	
	3.22×10^7	87.4	
	4.22×10^9	103.7	
av. ^d	1.7×10^8	93	310
Mo	2.28×10	43.7	
	1.56×10^3	59.3	
	5.02×10^4	71.7	
	6.76×10^4	73.4	
	2.47×10^6	85.6	
	3.13×10^8	102.7	
av. ^d	1.6×10^5	76	94
Ta	6.24×10^4	91.06	
	2.26×10^8	123.8	
av. ^d	2.8×10^6	106	0.06

TABLE 1 (continued)

Metal		A^a ($\text{mol m}^{-2} \text{s}^{-1}$)	E_a (kJ mol^{-1})	Relative reactivity ^b
W		1.72×10^2	59.6	
		7.82×10^3	75.4	
		1.22×10^4	77.1	
	av. ^d	1.2×10^3	68	11
Au		2.61×10^3	70.2	
		1.73×10^4	76.8	
	av. ^d	6.7×10^3	74	7.8
	SS ^e	1.17×10^6	96.6	
304L		9.02×10^5	97.3	
		5.10×10^6	102.5	
		6.80×10^6	103.5	
	av. ^d	2.6×10^6	100	0.43

^a Activation parameters derived from the initial portion of reaction with both liquid and vapor present.

^b Relative specific reactivity at 353 K calculated from average activation parameters.

^c Titanium reaction vessel only, background runs.

^d By least squares from the mean rates, see text.

^e Stainless steel, Fe:Cr:Ni 70%:19%:11%

ture range over which the activation parameters were measured depended not only on the inherent reactivity of the catalyst, but also on its surface area, and is 350–505 K. Activation parameters and relative specific activities for the transition-metal-catalyzed decomposition reaction of hydrazine are listed in Table 1.

For a series of background runs in titanium vessels, the standard deviations of the slopes of the Arrhenius plots are in the range 0.6–0.8 kJ mol^{-1} while the standard deviation of the mean of the activation energies for the four experiments is 2.4 kJ mol^{-1} or about 3%. However, for a non-linear equation such as the Arrhenius expression

$$k = A \exp(-E_a/RT) \quad (4)$$

where k = zero-order rate constant $\equiv$ rate, E_a = Arrhenius activation energy, A = Arrhenius pre-exponential factor, R = gas constant, and T = absolute temperature (kelvins), a more appropriate averaging technique is to calculate the activation parameters from the mean rate at each temperature as a function of temperature. The average activation parameters and relative reactivities shown in Table 1 were calculated in this manner. The temperature range over which the mean rates were calculated for each set corresponded to the onset and step temperatures.

Close inspection of the results indicates that among each series of experiments with a given catalyst, a large A value is generally accompanied by a higher activation energy. The differences are apparently not random experimental errors. This interdependence of the E_a and A values is commonly observed in heterogeneous kinetics [16].

DISCUSSION

The direct relationship between rate and surface area of added metallic materials as shown in Figs. 2 and 3 clearly implies that the decomposition of hydrazine is a surface-catalyzed reaction [17]. Under the high pressure conditions of the ARC experiment, surface coverage of the catalyst is expected to be nearly unity [6,9] which accounts for the similar reactivities observed when either liquid or vapor or both are present in the reaction vessel and the observed zero-order kinetics. Additionally, the response to surface area appears to be insensitive to the form (powder, turnings or foils) of added catalyst. This latter feature suggests that the results of ARC studies carried out with powders may be useful in the estimation of reactivities in hydrazine fuel systems constructed of bulk materials [4].

The correlation of the activation parameters for different samples of the same catalyst and among the different catalysts, in such a way that increased pre-exponential factors are countered by increased activation energies, is called the compensation effect, theta rule or isokinetic relationship [16,18]. Pooled data from Table 1, when plotted according to

$$\ln A = E_a/R\theta + \ln k_0 \quad (5)$$

provide a reasonable compensation plot (Fig. 4) with a compensation temperature $\theta = 445$ K.

A major source of scatter from the compensation line for the different catalysts is the error associated with specific surface area measurements (by geometrical measurements of foils or BET measurements of powders and turnings). The value of the specific surface area is incorporated in the pre-exponential term A . Much less scatter is shown by a limited data set for which these associated systematic errors are more or less constant. Figure 5 shows the compensation plot for six samples of molybdenum catalysts, including both 3–7 μm and $-200/+325$ mesh powders where $\theta = 432$ K.

The term "compensation effect" is most commonly used to describe the relationship between pre-exponential terms and activation energies for a series of closely related reactions. In linear form, the relationship is expressed as eqn. (5). An "isokinetic relationship" implies not only conformity to eqn. (5), but requires that there exists a temperature T_{iso} at which all rates are equal. As pointed out by Agrawal, random experimental errors can cause a "false compensation effect" [18]. A kinetically significant compensation

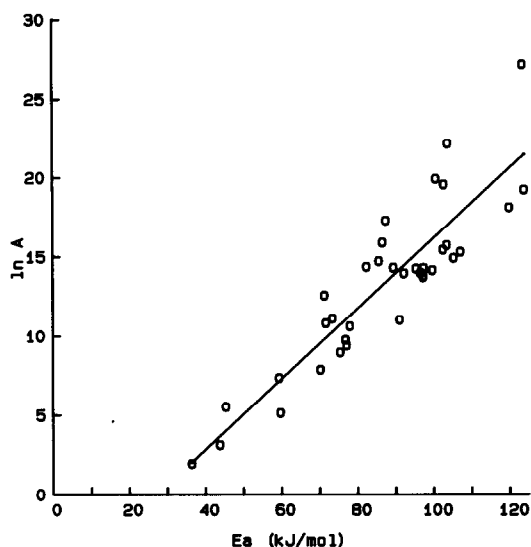


Fig. 4. Compensation relationship for the transition-metal-catalyzed hydrazine decomposition. Data from individual runs in Table 1, $\theta = 445$ K.

effect requires an isokinetic relationship and that $T_{\text{iso}} = \theta$. The test for a true isokinetic relationship in the metal-catalyzed hydrazine decomposition is shown in Fig. 6, which shows that the rates for all the members of a closely related set (molybdenum) substantially coincide at one temperature, $T_{\text{iso}} = 430$ K. The isokinetic temperature of 430 K for the molybdenum data agrees

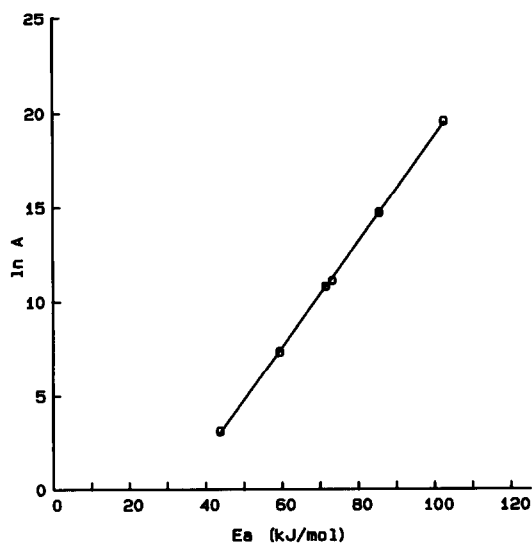


Fig. 5. Compensation relationship for molybdenum-catalyzed hydrazine decomposition, $\theta = 432$ K.

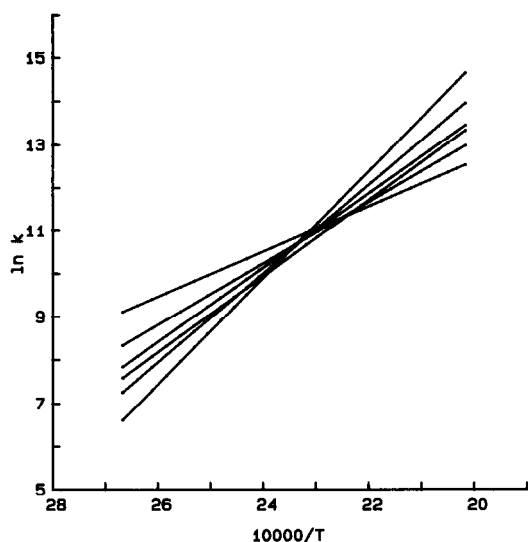


Fig. 6. Isokinetic relationship for molybdenum-catalyzed hydrazine decomposition. Arrhenius lines calculated from activation parameters in Table 1, $T_{\text{iso}} = 430$ K.

well with the compensation temperature, $\theta = 432$ K, determined from the slope of Fig. 5. The molybdenum data set was chosen to minimize scatter due to specific surface area measurement errors.

The compensation effect expressed in eqn. (5) can be combined with the Arrhenius relationship, eqn. (4), into a single relationship, which describes the surface shown in Fig. 7:

$$\ln(k/k_0) = (E_a/R)(1/\theta - 1/T) \quad (6)$$

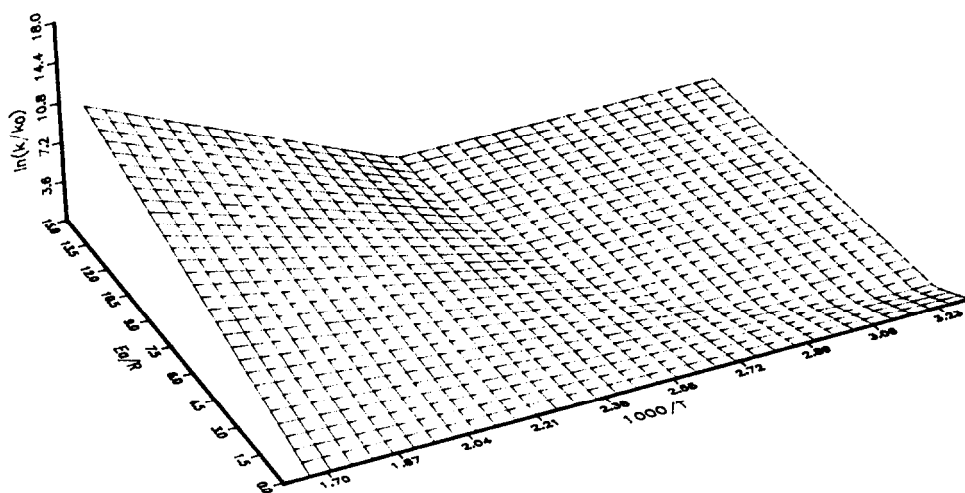


Fig. 7. Surface plot of $\ln(k/k_0) = E_a/R (1/\theta - 1/T)$ with $\theta = 430$ K.

where: k = zero-order rate (constant) at T , k_0 = zero-order rate (constant) at θ , θ = compensation temperature (Kelvin) and E_a = activation energy.

An important caveat accruing from eqn. (6), is that activities of the various catalysts depend not only on the activation energy, but also on the difference between the temperature of comparison and the compensation (or isokinetic) temperature.

In the development of an understanding of the catalyzed decomposition of hydrazine, measurements of the activities of various catalytic materials have seen considerable work. In an early study, Eberstein and Glassman [19] reported the activation energies for many of the transition-metal catalysts determined in a flow reactor. More recently, Volter and Leitz [7] reported kinetic parameters for chromium (87 kJ mol^{-1}), manganese (62 kJ mol^{-1}), iron (57 kJ mol^{-1}), tungsten (60 kJ mol^{-1}), rhenium (57 kJ mol^{-1}) and osmium (53 kJ mol^{-1}) in a low pressure flow system (10 Torr, 330–550 K). These results compare favorably with ARC measurements for tungsten and chromium but are appreciably different for iron. The data indicate a compensation relationship with $\theta = 456 \text{ K}$. The iron data deviates significantly from the compensation line.

The current ARC study gives a decreasing order of specific activities as: $\text{Co} > \text{Ni} > \text{Mo} > \text{V} > \text{Fe} > \text{W} > \text{Au} > \text{Ti} > 304\text{L} > \text{Cr} > \text{Ta}$

at 353 K, calculated from the “average” activation parameters (Table 1). The comparison temperatures of 353 K is about 100 K lower than the isokinetic temperature, lies within the liquid range of hydrazine and represents a reasonable temperature which might be reached by a hydrazine fuel system in failure.

If instead the catalysts are listed by increasing activation energy, the following order is obtained:

$\text{Co} < \text{W} < \text{Mo} < \text{Au} < \text{V} < \text{Ni} < \text{Ti} < 304\text{L} < \text{Cr} < \text{Ta} < \text{Fe}$.

Particularly notable are the changes in the rankings of iron and nickel. Although iron exhibits the highest activation energy among these metals, the compensating effect of a large pre-exponential results in appreciable reactivity. The same effect operates for nickel. Attempts have been made to correlate the catalytic activities of the various metals as catalytic agents in the hydrazine decomposition with parameters related to d-shell electron occupancy; however, these attempts have not led to any correlations with predictive usefulness [20,21].

Comparison of specific activities is complicated not only by selection of the comparison temperature but also by the uncertainty of the exact nature of the metal or alloy surface under these “real” conditions. The oxide surface layer can vary in composition and extent depending upon the surface treatment and prior exposure [22]. The metal surface preparation procedure used in this study is an attempt to produce uniform surfaces that simulate those formed by exposure to hydrazine under ambient conditions.

The catalyst pre-treatment protocol and the hold times at extended temperatures during wait-search ARC instrument cycles are expected to clear the surface reductively of the ambient-oxide layer for some materials. The hydrazine reduction of the oxides of cobalt, nickel, molybdenum, iron, tungsten and gold proceeds exothermically. These surfaces are observed to be the most reactive of the catalytic surfaces studied. On the other hand, the oxides of titanium, chromium, vanadium and tantalum are not exothermically reduced by hydrazine under the ARC conditions and the catalytic activity of these materials may actually be due to the surface-oxide layer. This hypothesis accounts for the low activity of the Fe:Cr:Ni alloy, 304L stainless steel. The ambient surface of 304L stainless steel consists of several layers, the outermost enriched in chromium oxide [23]. The reactivity of 304L then reflects that of the chromium-rich surface-oxide layer rather than that of iron or nickel in the bulk.

From a mechanistic point of view, the surface binding energies of N- and H-adatoms, as well as amido and imido groups, on metal surfaces have been shown to play a significant role in determining specific catalytic reactivities in ammonia synthesis [14]. These energies are not available for most materials nor are they easily measured [24]. However, the heats of formation of the metal oxides are readily available [25] and are, in a general way, related to the more fundamental chemisorption energies of nitrogen and hydrogen [26,27]. Our working hypothesis is that the catalytic activities are inversely related to the binding energies of N-adatoms. In the absence of data for N-adatom binding energies, we suggest the use of the heat of

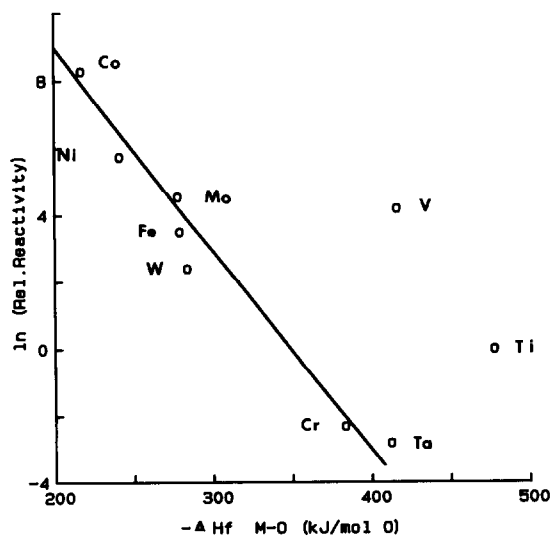


Fig. 8. Relative specific activity of transition metal catalysts for hydrazine decomposition as a function of ΔH_f of the metal oxide (per O atom).

formation of the metal oxide, ΔH_f per O atom, as a numerical substitute. For those surfaces expected to be oxide-free metals, the correlation shown in Fig. 8 is excellent. For the surfaces expected to be oxide coated, the correlation is less satisfying. Both titanium and vanadium are more reactive than the empirical correlation would suggest. Since the chemistry of both elements is dominated by multiple valence states, surface restructuring due to exposure to the reducing reaction conditions may involve stabilization and participation of lower oxidation state oxides [28]. Matloob has suggested that copper adsorbs hydrazine molecularly under conditions such that both iron and nickel dissociatively adsorb hydrazine [6]. By implication gold may also adsorb molecularly.

CONCLUSIONS

In conclusion, this work demonstrates that accelerating rate calorimetry can be used to characterize the surface-dependent transition-metal-catalyzed decomposition reaction of hydrazine. These observations present a new and useful application for the ARC in the field of heterogeneous catalysis. The results of this study hold promise for addressing problems associated with the selection of materials for use in hydrazine applications. Additional work is underway to explore the surface chemistry more fully and to develop an understanding of the systematic trends in the reactivities of the transition metals and their alloys in the catalytic decomposition reactions of hydrazines.

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