JOURNAL OF CATALYSIS 28, 116–123 (1973)

Catalyst Screening Using a Stone DTA Apparatus

I. Oxidation of Toluene Over Cobalt–Metal-Oxide Catalysts

K. PAPADATOS AND K. A. SHELSTAD

Faculty of Engineering Science, The University of Western Ontario,
London 72, Ontario, Canada

Received June 20, 1972

A method is presented for determining the activity of catalysts based on measurement of the temperature rise in a sample of the catalyst weighing a fraction of a gram. A Stone DTA apparatus was used in the experimental work. The reaction studied was the oxidation of toluene over 10 cobalt–metal-oxide catalysts. The activity of each catalyst was found to be directly proportional to the steady-state temperature rise in the sample, a fact which simplifies considerably the determination of activity. Activation energies were obtained for 9 of the 10 catalysts in the temperature range where the activity was stable. The determination of activity can be made without carrying out a product analysis, a fact which is useful for certain types of catalyst screening studies.

NOMENCLATURE

A_c	heat transfer area (cm^2)
α	activity [moles/(g sec)]
C_p	specific heat capacity of products [cal/(mole °K)]
$C_p{}^0$	specific heat capacity of reactants [cal/(mole °K)]
E	activation energy (cal/mole)
F	flow rate of products (moles/sec)
F^0	flow rate of reactants (moles/sec)
h	overall heat transfer coefficient [cal/(sec cm^2 °K)]
ΔH_R	enthalpy of the reaction (cal/mole)
k_0	Arrhenius frequency factor
n	number of measurements
R	gas constant [cal/(mole °K)]
T	temperature of the catalyst (°C)
T^0	temperature of the cell (°C)
T'	reference temperature (°C)
$\Delta T =$	$T - T^0$
$\Delta T_s =$	$T - T^0$ at steady state
V	flow rate of reactants (ml/sec)
W	mass of catalyst (g)
x	mole fraction of toluene in the product or conversion of toluene
x^0	mole fraction of toluene in the reactants

INTRODUCTION

Microreactors, such as that used by Kokes, Tobin and Emmett (*1*), have been widely used in the study of chemical reactions catalysed by solids. This paper reports on another design for such a reactor, one which makes use of the temperature rise in a sample of catalyst as a measure of the catalyst activity.

Use of the temperature rise in a layer of catalyst to determine its activity has been suggested by a number of authors (*2*–*5*). The method appears to be particularly useful for the screening of catalysts since it is rapid, can be done without carrying out a product analysis, and can also give information on catalyst stability and the effect of poisons. Many questions concerning the method, however, have not been answered adequately in the literature.

The studies reported in this paper are an attempt to shed light on some of these questions. For this purpose a Stone differential thermal analysis (DTA) cell was used to screen a number of cobalt–metal-oxide catalysts for the oxidation of toluene.

METHODS

Figure 1 is a block diagram of the apparatus used in the experiments. A stream of air from a cylinder was diverted in part through a bubbler containing toluene in order to prepare the feed gas. An arrangement of two 4-way valves and one 6-way sampling valve was used for sampling either the feed or product gases and for flushing the DTA cell with nitrogen. Analysis of the gas samples was by chromatography using helium as the carrier gas.

The Stone DTA unit consisted of the sample holder (model SH-12BE2-SSZ), furnace platform (model JP-202) and recorder controller (model LB-202F). Figure 2 shows that the sample holder is essentially a small metal block containing two cavities—the reference cavity filled with an inert solid and a sample cavity which contains a small amount of the catalyst being studied. In the arrangement for DTA studies a dynamic gas flows continuously through the two cavities. However, in the experiments to be described here flow through the reference cavity was blocked off. A differential thermocouple senses the difference in temperature between the two cavities and provides the signal which is interpreted in terms of the catalyst activity.

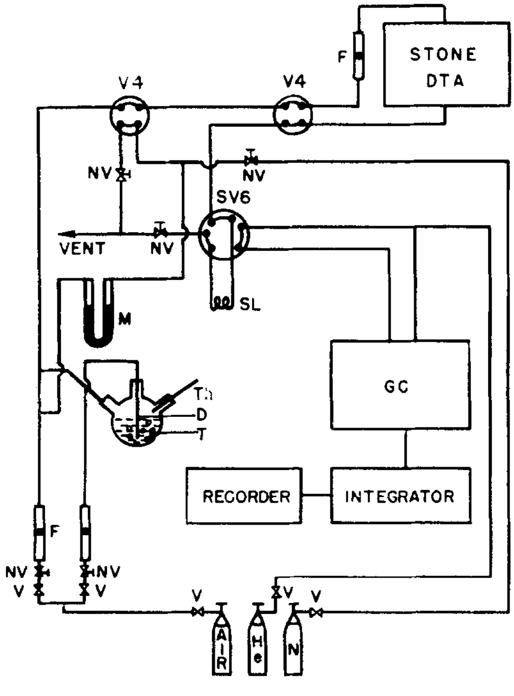

FIG. 1. Apparatus for catalytic studies using a Stone differential thermal analysis instrument.

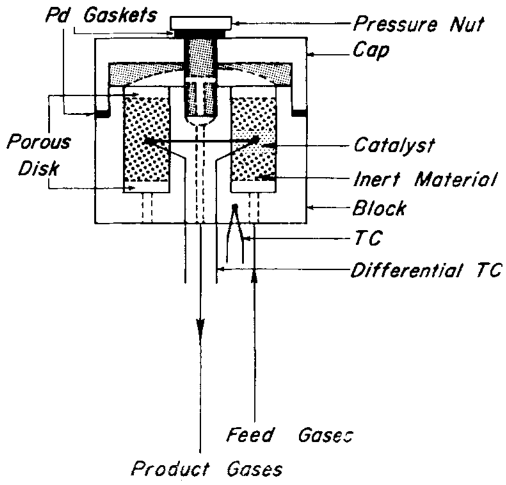

FIG. 2. Sample holder of Stone DTA instrument.

The gas chromatograph was a Varian instrument—model 1860-1 with recorder model 20 and electronic integrator model 480. The two columns of the chromatograph were made of ¼-in. stainless steel tubing packed with Poropak-Q. The reference column was 2 ft long and the analyzing column 4 ft long. Air and carbon dioxide were determined at room temperature, water during programming at 20°C/min, and toluene at 220°C.

Ten catalysts were prepared by thermal decomposition of the precipitated hydroxides using the procedure of Andrushkevich *et al.* (*6*). The nominal composition of each catalyst is listed in Table 1.

The procedure used in a typical experiment was as follows. The DTA cell was flushed with nitrogen, the instruments and air flow were turned on, and the system was allowed to become stable. A run was started by switching the feed to the DTA cell and having the product gases pass through the sampling valve. The temperature changes which took place within the layer of catalyst were recorded as a thermogram. With experimental conditions kept constant the temperature within the

TABLE 1
COBALT-METAL-OXIDE CATALYSTS[a]

No.	Catalyst formula	Drying Time (hr)	Drying Temp (°C)	Calcination Time (hr)	Calcination Temp (°C)
1	Co_3O_4	10	145	4	410
2	$NiCo_2O_4$	12	145	4	410
3	$Ni_{0.8}Co_{2.2}O_4$	14	145	4	410
4	$Ni_{0.5}Co_{2.5}O_4$	12	145	6	400
5	$Ni_{0.2}Co_{2.8}O_4$	15	120	6	400
6	$CuCo_2O_4$	8.5	125	14.5	350
7	$Cu_{0.8}Co_{2.2}O_4$	16	125	6	350
8	$Cu_{0.5}Co_{2.5}O_4$	18	125	4	350
9	$Cu_{0.2}Co_{2.8}O_4$	15	125	6	405
10	$ZnCo_2O_4$	14	125	6	400

[a] Prepared according to Andrushkevitch *et al.* (*6*). Composition nominal.

catalyst layer eventually reached a steady value. At this point the product gases were sampled and analyzed. The run was either repeated or the cell temperature was changed in preparation for another run.

MATHEMATICAL ANALYSIS

Consider the sample of catalyst in the DTA cell in contact with a steady flow of reactants and with one junction of the differential thermocouple imbedded in the layer. An enthalpy balance is written around the catalyst sample assuming its temperature has reached the steady-state value T.

$$\text{enthalpy entering} = F^0C_p{}^0[T^0 - T'], \quad (1)$$

$$\text{enthalpy generated} = -[F^0x^0 - Fx]\Delta H_R, \quad (2)$$

$$\text{enthalpy leaving} = FC_p[T - T'] + hA_c[T - T^0]. \quad (3)$$

Writing the balance, simplifying for a dilute feed, and rearranging terms results in the following equation:

$$[F^0C_p{}^0 + hA_c][T - T^0] = -F^0[x^0 - x]\Delta H_R. \quad (4)$$

The activity of the catalyst at temperature T is defined as follows:

$$\alpha = \frac{F^0[x^0 - x]}{W}. \quad (5)$$

From (4) and (5) the following simple relationship is obtained:

$$\alpha = K\Delta T_s, \quad (6)$$

where

$$K = -\frac{F^0C_p{}^0 + hA_c}{\Delta H_R W},$$

$$\Delta T_s = T - T^0.$$

Equation (6) implies that the activity of the catalyst is proportional to the steady-state temperature rise ΔTs of the sample of catalyst and to the factor K.

THERMOGRAMS

In the present work two types of thermograms were observed as illustrated in Fig. 3 for a 50 mg sample of $Cu_{0.8}Co_{2.2}O_4$. Each thermogram began with a sharp peak which was due to the transient temperature gradients formed when the reactants first made contact with the sample. This was followed by the tailing of the thermogram which was either a steady decrease of ΔT to a low, constant value or an almost constant value of ΔT after the sharp peak. With every catalyst used in this study the constant ΔT immediately after the sharp peak was observed only at the higher cell temperatures. At lower temperatures a slowly decreasing ΔT with time was always observed after the sharp peak.

The theoretical analysis resulting in Eq. (6) was based on the assumption of a constant temperature T of the catalyst sample. This analysis is expected to be valid, never-

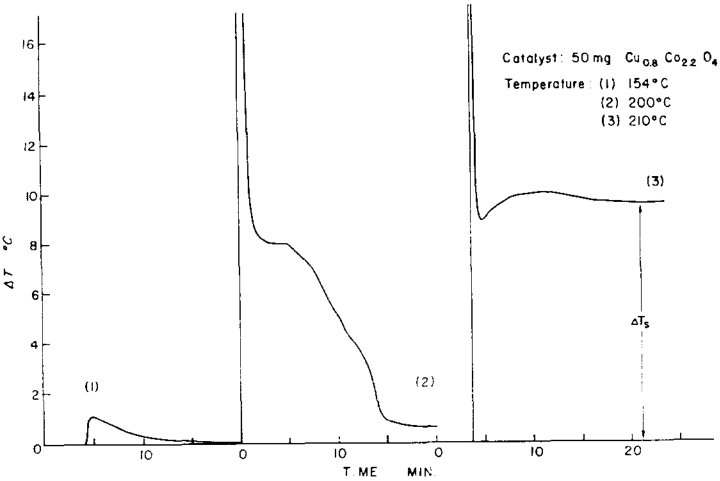

Fig. 3. Thermograms for oxidation of toluene over a Cu/Co-oxide catalyst.

theless, for the entire portion of the thermogram which follows the sharp peak and not only for just that section where T is constant.

Deactivation of the catalyst is thought to be the cause of the decrease in ΔT shown by the low temperature thermograms. This would probably result from accumulation of reaction products on the surface rather than from physical changes in the catalyst itself.

Results and Discussion

All the data obtained with the 10 catalysts over a range of temperatures are presented in Table 2. This table shows that the difference in temperature of the catalyst and of the cell block was usually quite small, varying from a fraction of a degree to the highest value in runs 6 and 7 for $CuCo_2O_4$ of 13.4°C.

Equation (6) indicates that the activity α is expected to be directly proportional to ΔT_s but that the coefficient K need not be a constant since it is possible for ΔH_R to vary. In a first test of this relationship the data for each catalyst were plotted as α vs ΔT_s. The plots obtained were highly linear, passing through the origin, and gave values for K which did not differ greatly for the different catalysts.

It thus appears that for oxidation of toluene over cobalt–metal-oxide catalysts the variation in ΔH_R is not large, perhaps because the reaction is principally one of complete oxidation. All the data were therefore placed on a single graph* as shown in Fig. 4. The line placed through the data points by a least squares calculation gives

$$\text{slope} = K = 0.97, \quad y\text{-intercept} = 0.27,$$
$$\text{correlation coefficient} = 0.96.$$

The fact that K is a constant for a particular catalyst and chemical reaction makes the technique simple to use for purposes of catalyst screening. K can be determined by a single measurement of the reactant conversion and ΔT_s at some temperature T. The activity of the catalyst at other temperatures can then be obtained by simply measuring ΔT_s at these other temperatures. Since the DTA cell temperature can be quickly changed and stabilized the activity determinations over a range of temperatures can be determined in a matter of minutes.

Relative activities can be determined even more quickly since the value for K is not required. The activity of a particular catalyst at a temperature T_2 relative to that at T_1 is the same as the ratio of the two steady-state temperature differ-

---

* The authors are indebted to a reviewer for this suggestion.

TABLE 2

Oxidation of Toluene Over Cobalt–Metal-Oxide Catalysts[a]

Cell temp (°C)	ΔT_s (°C)	Toluene conversion x	Activity α (moles/g sec × 10^7)	Cell temp (°C)	ΔT_s (°C)	Toluene conversion x	Activity α (moles/g sec × 10^7)	Cell temp (°C)	ΔT_s (°C)	Toluene conversion v	Activity α (moles/g sec × 10^7)
		Co_3O_4[b]				$Ni_{0.2}Co_{2.8}O_4$				$Cu_{0.5}Co_{2.5}O_4$	
152.0	0.00	0	0	202.0	0.00	0	0	150.0	0.00	0	0
200.0	0.15	0.018	0.17	238.0	0.80	0.005	0.95	198.0	0.20	0	0
220.0	0.35	0.036	0.33	250.0	7.00	0.433	6.33	209.0	1.40	0.081	1.12
230.0	0.40	0.036	0.33	251.0	6.60	0.430	6.29	215.0	7.40	0.510	7.05
242.0	0.80	0.171	1.60	262.0	8.80	0.590	8.60	222.0	9.40	0.650	8.98
250.0	3.10	0.415	3.89	272.0	9.00	0.733	10.7	232.0	9.60	0.687	9.50
263.0	4.00	0.477	4.46	285.0	8.40	0.817	11.9	244.0	10.80	0.792	11.0
272.0	4.00	0.527	4.95					263.0	9.80	0.930	12.9
						$CuCo_2O_4$		254.0	9.80	0.874	12.1
		$NiCo_2O_4$		152.0	0.00	0	0	244.0	9.20	0.817	11.3
151.0	0.00	0	0	200.0	0.50	0.009	0.13	232.0	7.40	0.570	7.87
202.0	0.00	0	0	210.0	0.90	0.106	1.50	222.0	5.60	0.356	4.93
222.0	0.20	0.020	0.28	215.0	9.00	0.650	9.20	215.0	3.40	0.150	2.07
235.0	0.60	0.054	0.74	220.0	12.80	0.860	12.2				
247.0	0.60	0.086	1.18	232.0	13.40	0.867	12.3				
255.0	4.50	0.502	6.92	243.0	13.40	0,917	13,0				
264.0	6.10	0.638	8.80								
274.0	8.10	0,732	10.1								

	$Ni_{0.8}Co_{2.2}O_4$				$Cu_{0.8}Co_{2.2}O_4$				$Cu_{0.2}Co_{2.8}O_4$		
150.0	0.00	0	0	200.0	0.60	0.049	0.71	150.0	0.00	0	0
200.0	0.10	0.023	0.33	210.0	9.40	0.646	9.43	205.0	0.30	0.013	0.19
221.0	0.30	0.034	0.49	211.0	6.40	0.557	8.13	220.0	6.40	0.414	5.93
250.0	6.60	0.455	6.56	220.0	8.40	0.660	9.64	233.0	9.20	0.542	7.75
258.0	9.80	0.573	8.26	222.0	10.60	0.710	10.4	244.0	10.60	0.654	9.36
266.0	10.80	0.607	8.75	233.0	10.00	0.785	11.5	259.0	12.00	0.768	11.0
280.0	11.80	0.695	10.0	249.0	10.80	0.840	12.3				
	$Ni_{0.5}Co_{2.5}O_4$								$ZnCo_2O_4$		
150.0	0.00	0	0					152.0	0.00	0	0
199.0	0.20	0.020	0.30					201.0	0.00	0	0
218.5	0.40	0.029	0.43					220.0	0.00	0	0
241.0	1.30	0.115	2.22					239.0	0.20	0.031	0.42
251.0	8.00	0.465	6.89					261.0	1.90	0.203	2.76
260.0	10.20	0.531	7.85					271.0	3.10	0.274	3.73
267.0	10.80	0.585	8.65								

---

[a] Catalyst weight = 50.0 mg; feed, 0.13% toluene in air; feed flow = 72 ml/min at 25°C, 1 atm.

[b] Feed flow = 48 ml/min at 25°C, 1 atm.

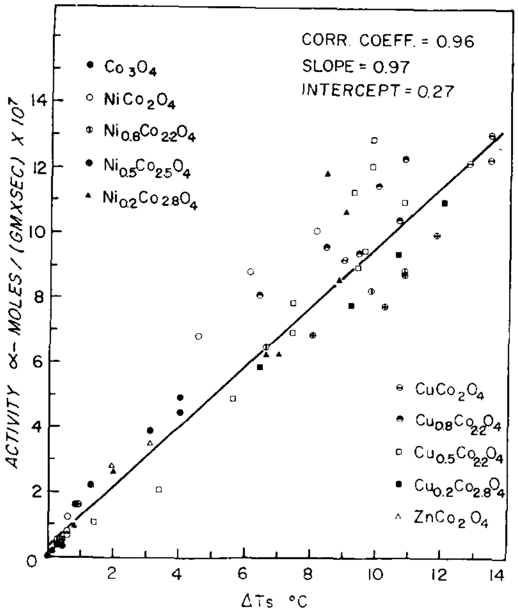

FIG. 4. Relationship between activity α and steady-state temperature rise ΔT_s.

ences, ΔT_{S2} and ΔT_{S1}, which can be rapidly measured using the DTA cell.

If information on product selectivity and activation energy is required then analysis of the product gases must be carried out. In the present study the analysis for CO_2 and the absence of partial oxidation products indicated a high degree of complete oxidation of the toluene. The results of the analysis for toluene are given in Table 2 in terms of the conversion x.

Correlation of the toluene conversion data at different temperatures was tested assuming the rate to be first-order in the toluene concentration and using the Arrhenius expression for the specific rate constant. Equation (7) is the integrated equation which was derived in the usual way:

$$\log_e[\log_e(1 - x)^{-1}] = -\frac{E}{RT} + \log_e\frac{k_0W}{V}. \quad (7)$$

The data plotted in accordance with Eq. (7) and correlated by a least squares calculation are shown in Fig. 5. Only data from those runs which showed a constant ΔT_S immediately after the sharp peak of the thermogram are included in Fig. 5. These are the higher temperature runs noted earlier where product adsorption was thought to be small.

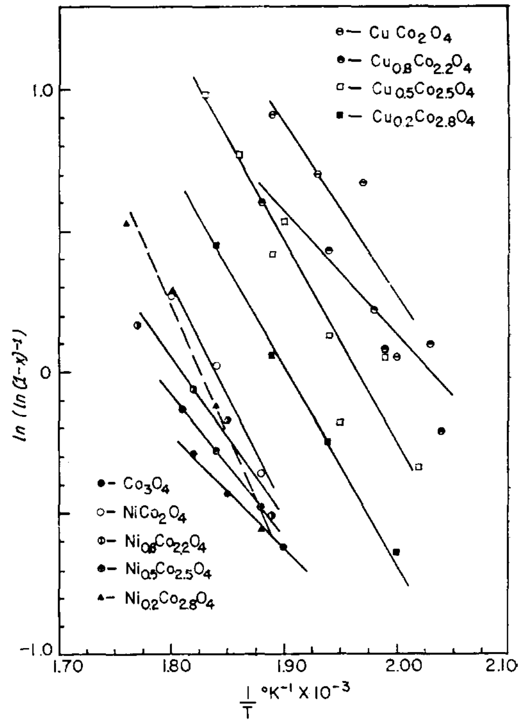

FIG. 5. Arrhenius plots for oxidation of toluene.

Figure 5 shows that reasonably straight lines were obtained for 9 of the 10 catalysts. No correlation for $ZnCo_2O_4$ was obtained since all the thermograms obtained for this catalyst showed the activity decreased with time. Values for the activation energy E are listed in Table 3.

TABLE 3
ACTIVATION ENERGIES FOR OXIDATION OF TOLUENE

Catalyst	E (kcal/mole)
Co_3O_4	8.1
$NiCo_2O_4$	15.6
$Ni_{0.8}Co_{2.2}O_4$	10.9
$Ni_{0.5}Co_{2.5}O_4$	9.9
$Ni_{0.2}Co_{2.8}O_4$	17.8
$CuCo_2O_4$	12.9
$Cu_{0.8}Co_{2.2}O_4$	8.9
$Cu_{0.5}Co_{2.5}O_4$	11.6
$Cu_{0.2}Co_{2.8}O_4$	13.4
$ZnCo_2O_4$	—

CONCLUSIONS

1. The activity of 10 cobalt–metal-oxide catalysts for the oxidation of toluene have been shown to be directly proportional to the steady-state temperature rise in a small sample of each catalyst.

2. Activities determined by temperature-rise measurements are useful for catalyst screening studies since a time-consuming product analysis is not required.

3. The method can also be used to give information on activation energies and catalyst stability.

ACKNOWLEDGMENTS

The work was supported financially by the Ontario Ministry of the Environment, Air Management Branch, and by a Province of Ontario Fellowship to K.P. The paper is based on the M.E.Sc. thesis in Chemical Engineering of K.P.

REFERENCES

1. KOKES, R. J., TOBIN, H., JR., AND EMMETT, P. H., *J. Amer. Chem. Soc.* **77**, 5860 (1955).
2. STONE, R. L., AND RASE, H. F., *Anal. Chem.* **29**(9), 1273 (1957).
3. LOCKE, C. E., AND RASE, H. F., *Ind. Eng. Chem.* **52**(6), 515 (1960).
4. STONE, R. L., *Anal. Chem.* **32**(12), 1582 (1960).
5. KARL, H., (*Glas.-Instrum.-Tech.*) *Fachz. Lab.* **14**, 403 (1970).
6. ANDRUSHKEVICH, T. V., BORESKOV, G. K., POPOVSKII, V. V., PLYASOVA, L. M., KARAKCHIEV, L. G., AND OSTAN'KOVITCH, A. A., *Kinet. Catal.* (*USSR*) (Eng. trans.) **9**(6), 1022 (1968).