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INVESTIGATION OF CATALYTIC ACTIVITIES BY DIFFERENTIAL THERMAL ANALYSIS

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Abstract

A calorimetric method is proposed to evaluate the catalytic activity of a solid catalyst with respect to the exothermic oxidation of Volatile Organic Compounds (VOC).

This method employs a differential thermal analyzer in which an inert reference and a catalytically active sample are both fluxed at a constant rate with a reactive gaseous mixture composed of an inert gas (N_2 90% vol.), oxygen and VOC, the last typically 900 to 5000 ppm. While the temperature is varied according to a predefined cycle, the output signal due to the exothermic reaction on the catalyst is continuously recorded. The design of the test chamber, the amount of catalyst, the shape of the holders and finally the flow rate and composition of the gaseous mixture should be carefully selected in order to achieve reproducible results.

Keywords: catalyst

Introduction

Many calorimetric techniques have been suggested and described in the literature to detect the heat evolved during catalyzed exothermic reactions. The heat evolved can be directly related to the rate of the reaction which occurs inside a test chamber of a reactor filled with the catalyst under examination. The equipment usually allows controlled variation of the operational parameters, as temperature, flow rate and concentration of the reactants.

These methods can be employed with homogeneous as well as heterogeneous catalysts in a reaction medium that can be liquid or gaseous. The method proposed by Schwartz *et al.* [1] involves, for example, the measurement of the temperature of a solid catalyst in the oxidation of selected organic compounds in the gaseous state, whilst the temperature is gradually varied according to a predefined cycle. In the equipment devised by Landau *et al.* [2] calorimetric data from a laboratory reaction calorimeter operated in the liquid phase, were used in predictive kinetic models which allowed simulation of the temperature profiles in a pilot plant.

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When a solid catalyst and a gaseous reactive mixture are exposed to a linear temperature ramp, the heat generated by the exothermic reaction may not be immediately transferred by conduction-convection from the catalyst surface, thereby increasing noticeably the catalyst surface temperature above the value required by the programmed cycle. Under these circumstances the heat generation curve as a function of catalyst temperature exhibits a typical sigmoid shape, with an abrupt change from the region of kinetic control to that of diffusive control [2]. In these cases the kinetics of the chemical reactions must be thoroughly investigated to describe the reaction mechanism [3].

The method described in this paper employs small amounts of a solid catalyst (3 to 10 mg) and does not require that the reactive gaseous mixture is forced through the catalyst bed in a reaction chamber, but simply allows it to diffuse onto the active surface of the catalyst. This technique permits rapid measurement of the characteristic parameters of a heterogeneous catalyst, as the ignition temperature, apparent activation energy and others.

Experimental

The method described employs a commercial thermal analyzer (Setaram 1992), featuring DTA as well as TG capabilities, in order to measure the catalytic activity of a solid catalyst. In a standard test the temperature is varied in the measuring chamber of the calorimeter according to a predefined cycle, whilst a sample of the catalyst and an inert reference are fluxed at constant rate with a reactive mixture. This reactive gaseous mixture is composed of an inert gas (90% vol. N_2), oxygen (10%) and a volatile organic compound (VOC), typically 900 to 2000 ppm, whose enthalpy of oxidation is to be provided by the differential calorimeter.

The construction and the geometric characteristics of the measuring chamber of the thermal analyzer, the shape and material of the sample and reference containers and the amount of catalyst are of paramount importance in determining the sensitivity and reproducibility of this particular analytical method. An elongated and small-diameter (1.5 cm) test chamber must be selected, in which the gaseous mixture necessarily streams downward, whilst the sample and reference, with their thermocouples arrangements, are hung on the electronic balance arm (Fig. 1), instead of being supported by it.

Since the reactive gaseous mixture is not forced through the catalyst, but flows around it, the reaction rate and the consequent heat flow are mainly controlled by diffusion processes, except at the earliest stages of the reaction.

For the same reason complete conversion of the incoming mixture cannot be achieved even at the highest temperatures applied, as part of the gas always avoids the sample or gets on the reference itself.

The temperature difference between the catalyst sample and inert reference (α-Al_2O_3, corundum) having the same mass is continuously monitored by two sets of three thermocouples, fitted in a receptacle under the holders (Fig. 1), as

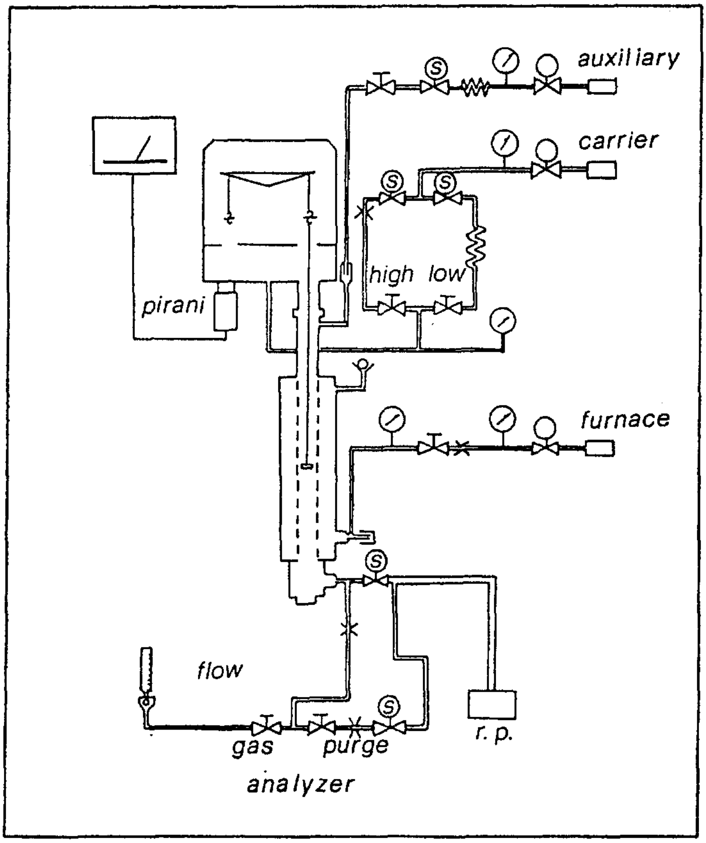

Fig. 1 Schematic drawing of the calorimeter test chamber. (S = gas switches; r.p. = rotary pump), (auxiliary = oxygen), (carrier = nitrogen + VOC), (furnace = protective gas for the heating elements: argon)

commonly found in DTA equipment. The holder material for low temperatures (up to 550°C) is aluminium, whilst for higher temperatures alumina is employed.

The sample and reference are hung on one arm of an electronic balance, so that the mass change of the catalyst can also be continuously monitored during the scan. The activity curves (mwatt=$f(T)$) are corrected by subtracting from them a blank curve obtained under the same operating conditions but in the absence of VOC. This corrected output signal of the equipment (mvolt difference between the two *emf* values) is transformed, according to a calibration curve, into net heat flow per unit mass of catalyst (mwatt mg^{-1}). This calibration curve was separately obtained through measurement of the area of the melting peak of organic substances with known heat of fusion (naphthalene, melting point 80.2°C, heat of fusion 35.06 cal g^{-1}; benzoic acid *m.p.* 122.4°C, 33.89 cal g^{-1}

and anthracene, *m.p.* 216.2°C, 38.70 cal g^{-1}) using the same holders, the same gas atmosphere and the same linear gas velocity but in the absence of VOC.

The operating conditions as the gas velocity, heating rate, VOC concentration and catalyst mass were separately varied in different runs in order to optimize the sensitivity of the test. The catalyst employed was a commercial product (ESCAT-24, Engelhart GmbH) composed of Pt 5% by weight on γ-alumina while the VOC was benzene in gaseous admixture with N_2. With the above catalyst we obtained a set of optimal operating parameters, valid for a wide range of catalysts, that can be described as follows:

1) Heating rate: from 0 to 5°C min^{-1} the Heat Flow (HF) response is independent of the heating rate, the HF curve is nearly reversible in cooling/heat cycles. At heating rates higher than 5°C min^{-1}, the system operates under temperature gradients, in non-steady-state conditions, the curves become less reversible and the sensitivity is consistently impaired.

2) Linear velocity of the gaseous phase: from 4 to 8 mm s^{-1} the best sensitivity is achieved, with the maximum around 6 mm s^{-1}. Higher rates promote non-laminar, turbulent flow thereby increasing heat exchange between sample and reference and lowering sensitivity. Lower fluxes impair sensitivity as the reactant feed is diminished.

3) Thickness of the catalyst layer in the holder: the sensitivity decreases as the layer thickness increases due to a temperature gradient between the reaction sites and detectors and possible heat transfer from active sample to inert reference. Best results are obtained at a thickness of 0.8 $\div$ 1.2 mm; smaller thickness means less catalyst and therefore less HF.

4) Oxygen to VOC ratio: this ratio is normally kept very high in order to promote complete oxidation of VOCs. A suitable composition of the reactive gaseous admixture is: $\approx$10% vol. O_2, $\approx$90% vol. N_2, 900 ppm vol. VOC.

A typical temperature program with noble metals as catalyst and benzene as Volatile Organic Compound consists of a ramp of 5°C min^{-1} from room temperature up to 400°C, that can be followed by a cooling ramp of 5°C min^{-1} down to 100°C (Fig. 2).

Under the above experimental conditions no change in mass is observed and the DTA curves can be divided into three regions, each with a defined temperature range. These ranges can be labelled as kinetic, diffusive and equilibrium regions, for clearness.

1) Kinetic region: the partial pressures of VOC in the pores and the quantity adsorbed on the active sites of the catalyst remain unchanged until the ignition temperature, about 135°C for C_6H_6 and Pt/Al_2O_3, is reached. During the subsequent period, of about 4 to 8 min, whilst the temperature increases by about 20 $\div$ 40°C, the VOCs adsorbed onto the catalyst surface rapidly react, and the HF curve typically shows a first exponential rise. These transient phenomena

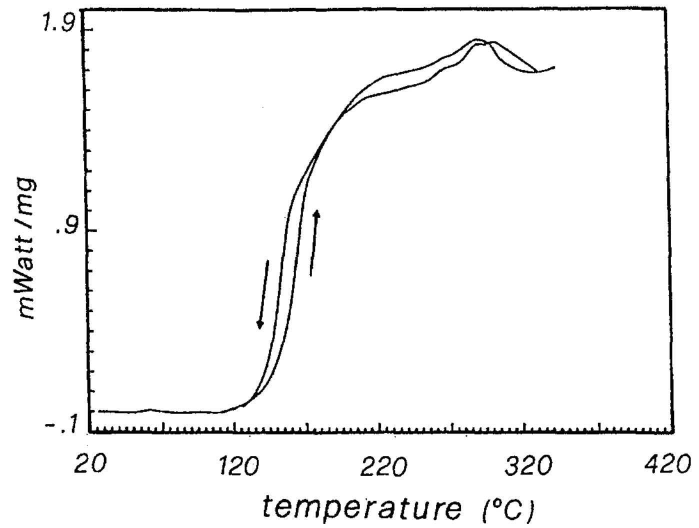

Fig. 2 Typical Heat Flow (HF) curve, for Pt on γ-Al_2O_3 catalyzing the oxidation of benzene

are more evident when highly active catalysts are employed or when autocatalytic oxidation occurs, as might be the case with e.g. ethyl acetate oxidation. In these cases the HF curve may show one single peak after the ignition (Fig. 3).

2) Diffusive region: after the first region the reaction rate is controlled mainly by the diffusion of reactants: if the heating rate is slow enough (less than 10°C min^{-1}), mass transfer and chemical reactions are much faster, so that the system goes through a series of states which can be considered as 'pseudo-stationary'. As a result, a second exponential rise occurs in the HF curve, whose calculated activation energy is markedly lower than that the first one.

3) Equilibrium region: after the diffusion-controlled region the reaction rate is limited by the total reactant feed over the catalyst surface and at the same time also by the adsorption equilibrium position. The reactant feed is determined by the ratio between the exposed area of the sample and the cross sectional area of the reaction chamber, by the flow rate and VOC concentration. The position of the adsorption equilibrium of VOC on the active surface of the catalyst is moreover shifted towards the gaseous phase as the temperature increases, thus lowering the quantity of VOC adsorbed and therefore the reaction rate. Indeed, during this third region HF normally slowly decreases with temperature.

The experimental data are in agreement with those obtained on the same catalyst by different technique (e.g. integral reactors with continuous chemical analysis of the product). For example, the ignition temperature obtained in a catalytic combustion reactor [4] with a 1000 ppm mixture only differs by 2°C (137°C instead of 135°C).

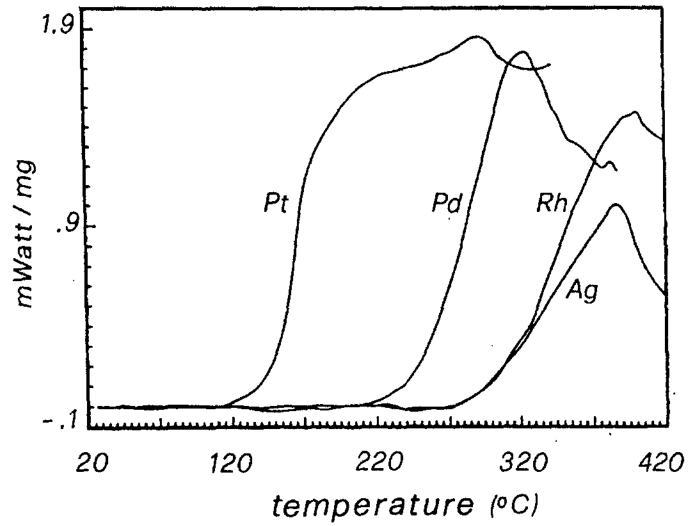

Fig. 3 Heat Flow (HF) curves for Pt, Pd, Rh, Ag on γ-Al_2O_3 catalyzing the oxidation of benzene

Our method has the additional advantage of fast comparative evaluation of catalytic activity in exothermic reactions (as VOC oxidation) on small amounts (8 to 20 mg) of catalyst. Indeed, a thermal activity curve can be obtained using a fully automated procedure in about 3 h. Moreover, the apparent Activation Energy is easily calculated by plotting log(Heat Flow) *vs.* $1/T$ and measuring the slope of the relative curve (Arrhenius plot).

High-temperature catalytic reactions (for example, oxidation of methane and halocarbons) can be investigate by this apparatus, due to its high temperature limits (over 1000°C).

Catalyst description and preparation

Once the experimental conditions were adjusted for best sensitivity and reproducibility with the aid of the commercial Pt/Al_2O_3 catalyst, the reliability of the method was confirmed on a series of noble metal catalysts, prepared in our laboratory.

The solid catalysts were obtained by wetting the support material (γ-alumina, AKZO Chemie, about 100 m^2g^{-1} of surface area), as supplied, with a solution of the noble metal followed by careful evaporation. The solutions were prepared by dissolving in acetone respectively

- Platinum (II) acetylacetonate (97% purity),
- Palladium (II) acetylacetonate (99% purity),
- Rhodium (III) acetylacetonate (97% purity)

(Aldrich Chem. Co) in amounts to get solutions, $5\cdot10^{-3}$ mol l^{-1}.

The mixtures of γ-Al_2O_3 and metal solutions were first dried in air at room temperature and subsequently slowly heated in air up to 400°C. After 30 min, the material was ground in an agate mortar.

For the Ag catalyst a $5\cdot10^{-3}$ mol l^{-1} solution was prepared by dissolving silver nitrate (purity min 99.8%, Merck and Co.) in distilled water. The amount of the noble metal corresponded to $1\cdot10^{-4}$ mol g^{-1} (Al_2O_3), whilst the concentration of the commercial catalyst (ESCAT-24) was 5% by weight.

A part of these solids was also reduced in a hydrogen stream (H_2 5% vol, Ar 95% vol) at 400°C in order to assure complete reduction of the metal. The thermocatalytic tests relating to benzene oxidation with the above method furnished the results listed in Table 1. The operating conditions are summarized in the same table.

Table 1 Experimental data of thermocatalysis under the following operating conditions: Heating rate: 5°C min^{-1}; mass of catalyst: 8 mg; linear flow rate: 6 mm s^{-1}; gaseous reactive mixture: ≈ 10% O_2; ≈ 90% N_2; 900 ppm vol. C_6H_6

Material	$T_{Ignition}$/°C	E_{att}	Max *HF*	Max *HF* (der. up)	Max *HF* (der. down)
Pt/γ-Al_2O_3	115	110	1.8	165	155
Pd/γ-Al_2O_3	210	160	1.7	275	255
Rh/γ-Al_2O_3	275	170	1.4	330	315
Pt/γ-Al_2O_3*R*	120*	–	–	165	155
Pd/γ-Al_2O_3*R*	175*	–	–	–	–
Rh/γ-Al_2O_3*R*	245*	–	–	–	–
Ag/γ-Al_2O_3	275	–	1.0	340	305
Ag/γ-Al_2O_3*R*	180*	–	–	–	–
ESCAT-24	120	135	0.7	135	135

* Apparent ignition temperature only in the first run (see text)

R Reduced material

The ignition temperature is defined as the temperature at which the first significant deviation of the *HF* curve from the baseline occurs.

E_{att} is the Apparent Activation Energy from the Arrhenius Plot (kJ mol^{-1})

Max *HF* is Maximum Heat Flow (mwatt mg^{-1})

Max *HF* (der. up) is the temperature of the highest derivative Heat Flow (d*HF*/d*T*) during the temperature increasing ramp.

Max *HF* (der. down) is the temperature of the highest derivative Heat Flow (d*HF*/d*T*) during the temperature decreasing ramp.

The slight difference between the two latter results gives clear evidence of the temperature homogeneity and justifies the assumption of pseudo-stationary states during the analysis.

Pt-based catalysts display the lowest ignition temperature and the highest HF, followed by Pd, Ag and Rh. The Pt supported on γ-Al_2O_3 prepared in this laboratory shows the same ignition temperature but a higher activity with respect to the commercial samples ESCAT 24, a fact that could be related to the higher specific area of the alumina employed as support.

The samples treated in a reductive atmosphere of Ar/H_2 show appreciable shifts towards lower temperatures in the HF curves from the non-reduced materials, but only in the first run after the reduction treatment. Successive runs were practically coincident with those obtained on the catalysts oxidized in air at 400°C. This fact could be related, in our opinion, to the solubility of molecular hydrogen in the noble metals employed. The combustion of hydrogen which remained dissolved in the noble metal after the reduction treatment could be responsible for the exothermic peak which was observed only in the first run after the reduction, which only apparently lowers the ignition temperature of the catalyst.

References

1 A. Schwartz, L. L. Holbrook and H. Wise, J. Catal. 21 (1971) 199.
2 R. Landau, D. G. Blackmond and H. H. Tung, Ind. Eng. Chem. Res., 33 (1994) 814.
3 Y. S. Matros, Unsteady Proc. in Cat. Reactors, Elsevier, Amsterdam 1985.
4 I. Mazzarino and A. A. Barresi, Catalysis Today, 17 (1993) 335.