

DSC–GC STUDIES ON THE OXIDATION OF CO OVER VANADIA CATALYSTS

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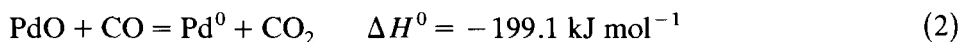
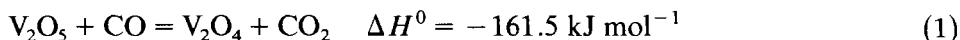
ABSTRACT

The oxidation of CO on unsupported, supported and Pd-doped vanadia catalysts has been studied in a coupled DSC–GC system. By the simultaneous determination of the conversion and the molar heat of CO₂ formation, calorimetric information revealing the partial reduction of the surface before the attainment of a steady state have been obtained.

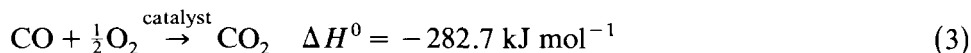
INTRODUCTION

In the last few years the reduction of CO emission has become one of the most urgent tasks of environmental hygiene. This is why nowadays the catalytic oxidation of exhaust and waste gases is brought, step-by-step, into general practice. A wide range of transition metals and their oxides may serve as catalysts in this reaction [1–3]. It is very probable, however, that under reaction conditions a recurrent oxidation–reduction of the metal occurs and the steady state is characterized by a stationary concentration of upper and lower valence states of the surface metal atoms.

Therefore, when using V₂O₅ or PdO/V₂O₅ as catalysts, the initial stages of reaction processes like



might be distinguished from the net catalytic oxidation:



by a precise determination of the reaction heats.

EXPERIMENTAL

The combined DCS–GC system which enabled work to be done both in pulse reactor (PR) and flow reactor (FR) operation mode is shown in Figs. 1a and 1b.

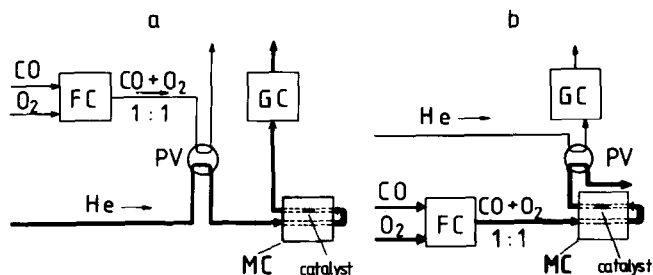


Fig. 1. The coupled DSC-GC system in pulse (a) and in fixed-bed flow reactor (b) modes. FC, Two-channel flow controller; GC, gas chromatograph; MC, measuring cell of the calorimeter; PV, pulsing valve.

In the original setup the measuring cell of the Setaram DSC 111 heat flux calorimeter is crossed by air-tight stainless steel tubes. In order to avoid undesirable wall effects, these tubes have been replaced by fused silica ones. One of them is blank and serves as a reference cell and the other is used as the sample cell, i.e. as a fixed-bed catalytic reactor.

The calorimeter was calibrated by measuring the melting heat of high-purity metals (In, Al). Gases were purified by molecular sieve absorbents and from the carrier He, traces of O_2 were removed by a special oxygen-absorbent.

In FR regime the flow rates for O_2 and CO were $10 \text{ cm}^3 \text{ (STP) min}^{-1}$ regulated by a Brooks type two-channel flow controller. In pulse reactor operation (PR) the flow rate of He was $40 \text{ cm}^3 \text{ min}^{-1}$ and the pulse volume for a 1 : 1 mixture of CO + O_2 was 0.86 cm^3 .

The catalysts studied are characterized as follows:

Catalyst (A): analytical grade V_2O_5 (Reanal): $s_0 = 3.0 \text{ m}^2 \text{ g}^{-1}$.

Catalyst (B): 10% V_2O_5 supported on Ketjen $\gamma\text{-Al}_2O_3$.

Catalyst (C): PdO/ V_2O_5 , impregnated as 0.28 wt.% PdCl₂ on a high-purity V_2O_5 (Merck, $s_0 = 4.9 \text{ m}^2 \text{ g}^{-1}$).

Catalyst (D): PdO/ V_2O_5 / Al_2O_3 , impregnated as 7% PdCl₂ on catalyst (B). Before the experiments all the catalysts were calcined in air at 720 K for 1 h, and oxidized in situ under O_2 flow, also at 720 K for 0.5 h.

RESULTS AND DISCUSSION

Kinetic investigations have revealed that Pd-doping resulted in a powerful increase of the catalytic activity. The order of activity, based on the temperatures required to effect the same conversion per unit weight was: (A) < (B) \ll (C) \approx (D). Thus, in pulse reactor mode, using 180 mg of catalysts (A), (B), (C) and (D) a conversion of 25% was achieved at 870, 770, 320 and 300 K, respectively. Therefore, in case of (C) and (D) the reaction was

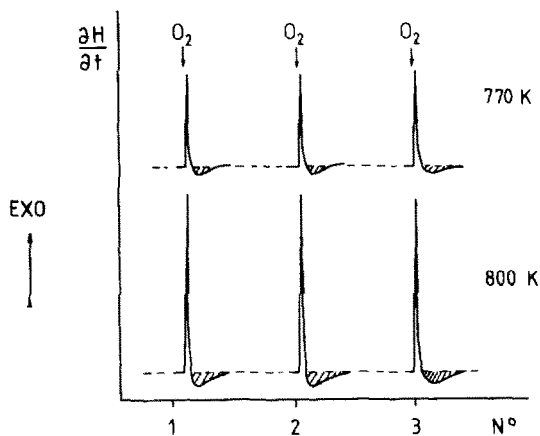


Fig. 2. Heat effects caused by subsequent pulses of $0.85 \text{ cm}^3 \text{ O}_2$ on catalyst (A).

studied in the range 300–450 K, whereas in case of catalysts (A) and (B) appreciable conversions ($\leq 1\%$) of CO to CO_2 were found only above 700 K. At these temperatures, however, the stoichiometry of the surface of V_2O_5 also becomes questionable. When pulses of pure O_2 were injected onto the catalyst, a fast exothermic effect followed by an endothermic peak with a relatively wide tail was observed (Fig. 2).

As Fig. 2 also indicates, the areas of the relevant exothermic and endothermic peaks are practically equal. Therefore the observed phenomenon very likely refers to a reversible uptake and release of O_2 while the pulse passes over the catalyst bed. (The observed shape of the GC peaks of O_2 after passage through the catalyst bed also supported this idea.) Therefore it is considered that at these temperatures and under He flow the surface of vanadia is a priori oxygen-deficient, which, when exposed to oxygen, immediately undergoes a reoxidation.

The actual oxygen deficit, i.e. the surface concentration of the V^{4+} ions in the He flow, may be estimated from the observed exothermic heat effects (ΔH_{ox}) if we suppose that by one pulse of O_2 , temporarily an almost complete reoxidation of the surface occurs. Considering that between 770

TABLE 1

The percentage fraction of surface vanadium(IV) atoms of V_2O_5 (sample A) under He flow at 770, 800 and 850 K, as deduced from the exothermal heat effect of the reversible O_2 uptake

T (K)	770	800	850
ΔH (J g^{-1})	-0.145	-0.233	-0.326
V^{4+} (surf) (%)	5.5	8.9	12.5

and 850 K the heat of the $2\text{VO}_2 + 1/2\text{O}_2 = \text{V}_2\text{O}_5$ reaction varies from -110.4 to -108.3 kJ mol^{-1} , and taking into account the specific surface and the weight of the sample as well as the structure of the basal (001) plane of V_2O_5 , the results given in Table 1 are obtained. Consequently, in inert gas atmosphere an appreciable proportion of surface vanadium exists in a lower valence state.

Flow reactor experiments

In FR operation, on catalysts (C) and (D) the steady state conditions characterized by a stabilized conversion (α) and a stabilized heat flux were readily achieved. In the presence of catalysts (A) and (B), however, a slow prolonged initial increase of the conversion and the heat flux was observed.

Typical results for catalysts (A) and (C) are presented in Fig. 3. We consider that on catalysts (A) and (B) the slow initial increase of the catalytic activity is caused by the slow reduction of V_2O_5 towards a more active surface layer. This might be an oxygen-deficient superstructure on a V_2O_5 matrix [4] or even a V_6O_{13} type surface phase. The latter was found to be more active than the stoichiometric V_2O_5 phase in catalytic oxidation of organic compounds [5-7].

Study of the initial stage by pulse technique

When subsequent pulses of $\text{CO} + \text{O}_2$ are injected onto catalysts (A) and (B), the conversion slightly increases with the pulse number, also indicating

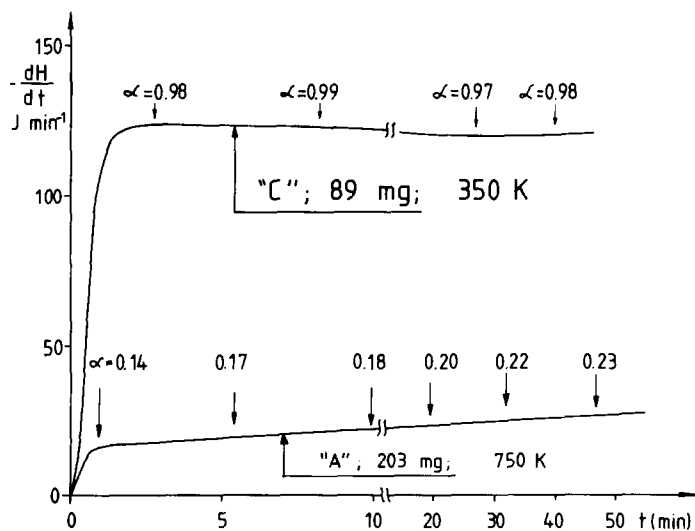


Fig. 3. The variation of the heat flux and the conversion (α) in FR. $v_{\text{CO}} = v_{\text{O}_2} = 10$ $\text{cm}^3 \text{min}^{-1}$.

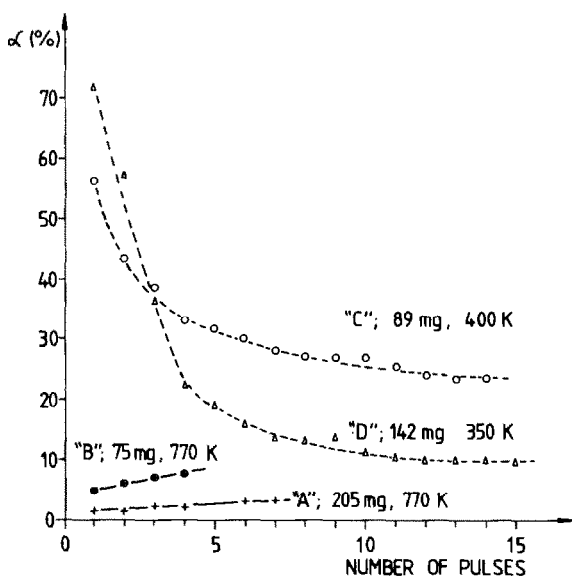


Fig. 4. The variation of α with the pulse number for catalysts (A), (B), (C) and (D).

that during the reaction the catalyst gradually becomes more and more active, as shown in Fig. 4.

In the case of the Pd-doped catalysts (C, D) an opposite phenomenon

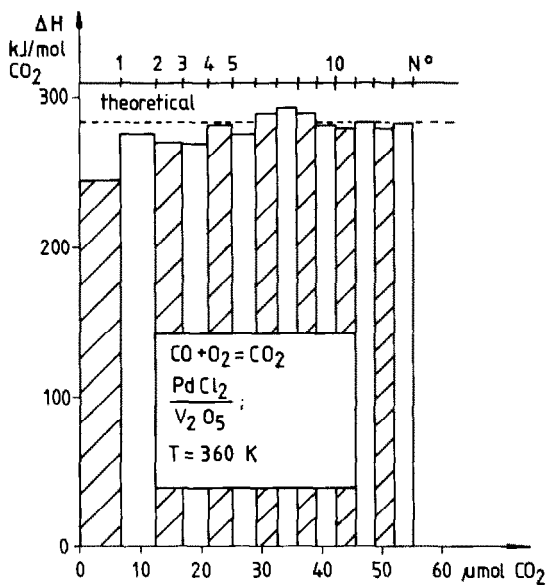


Fig. 5. Variation of the molar heat of CO_2 formation with the pulse number (N^0) on catalyst (C). $m = 257$ mg, $T = 360$ K.

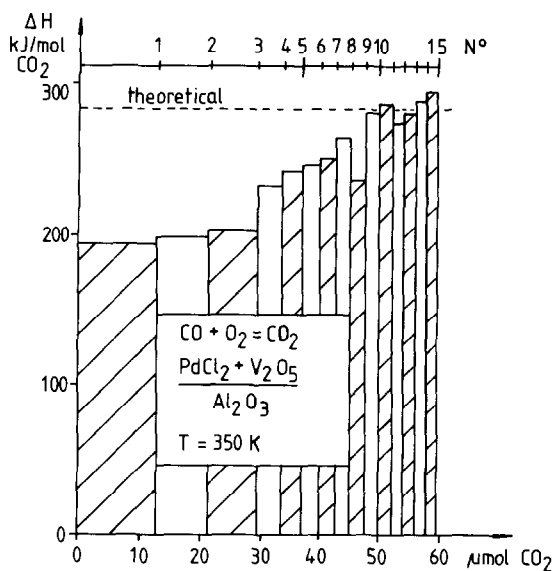


Fig. 6. Variation of the reaction heat in subsequent pulses on catalyst (D). $m = 142\text{ mg}$, $T = 350\text{ K}$.

occurs: the high initial conversions tend to become stable at a considerably lower level as can be seen in the same figure.

A simultaneous determination of the exothermic heat effect has revealed that on catalysts (A) and (B), where the reduction of the surface by reactions

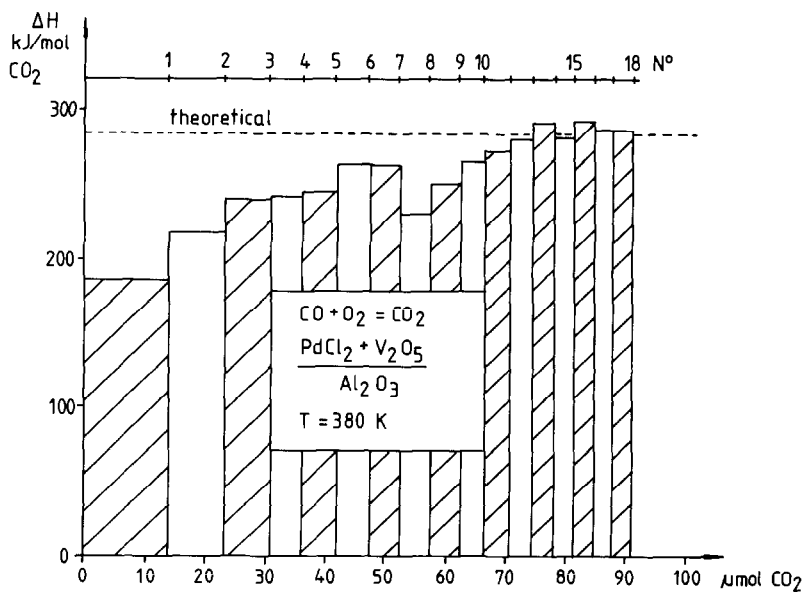


Fig. 7. The same as in Fig. 6 but for 380 K .

of type (1) is a relatively slow process, the heat of CO_2 formation is 280–290 kJ mol^{-1} , i.e. practically corresponds to that of the net catalytic oxidation. At the same time in the case of catalysts (C) and (D), the high initial conversions are accompanied with much lower reaction heats. Such results are shown in Figs. 5–7, where the molar heat of CO_2 formation is plotted against the amount of CO_2 already formed. These results suggest that in the initial stage, even with oxygen introduced in excess, lattice oxygens are also involved in the oxidation of CO by reactions of type (1) and (2). As a comparison of Fig. 5 with Figs. 6 and 7 shows, this phenomenon is more pronounced in the case of catalyst (D), which is of higher Pd-content (7%, as PdCl_2) than catalyst (C) doped only with 0.28% of PdCl_2 . After several pulses the surface concentration of the lower valence state metals approaches the quasi-steady state value, resulting in the stabilization of the conversion and the molar heat of CO_2 formation. As indicated, after this stabilization the reaction heats alter around the theoretical value referring to the net catalytic process.

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