Journal of Thermal Analysis, Vol. 33 (1988) 519–524

CHARACTERIZATION OF THE REDOX-REACTIVITY OF TRANSITION METAL OXIDES BY TEMPERATURE-PROGRAMMED LIMITED THERMAL DECOMPOSITION (TPLTD)

R. Dziembaj and *J. Surman*

FACULTY OF CHEMISTRY, JAGIELLONIAN UNIVERSITY,
KARASIA 3, PL-30-060 CRACOW, POLAND

The concept of labile lattice oxygen (LLO) as a consequence of the Mars-Van Krevellen model was reminded, and contrasted with the surface oxygen species. Methods of characterizing of the Me—O bond strength were reviewed emphasizing the temperature-programmed limited thermal decomposition (TPLTD). A series of $Ag_xV_2Mo_yO_z$ was characterized by TPLTD. Two forms of LLO were distinguished. The weaker form is independent on Ag-doping, in contrast to the stronger one. Activation energy of TPLTD of the stronger bound LLO was a linear function of the anion vacancy concentration.

Redox-model of the transition metal oxides ctalysts

The transition metal oxides (TMO) are well-known catalysts of many reactions. The long discussion about which oxygen form is the oxidizing agent finished in the alternative [1, 2].

The chemisorbed species (O^-, O_2^{2-}, O_2^-) cause the full oxidation (combustion). Therefore, the catalysts for the exhaust-pipe of motorcars consist of such metal oxides, which can easily regenerate these species on the catalyst surface during the catalytic reaction. It can be also the surface oxide phases of noble metals.

In case of the partial oxidation, e.g. the selective oxidation of benzene into maleic anhydride, the Mars-Van Krevellen mechanism takes place. This needs oscillation of the metal oxidation number (transfer of electrons) as well as the oxygen content (transfer of oxygen). In this connection there is the concept of labile lattice oxygen (LLO), which explains the deviation from the oxide stoichiometry in the course of the catalyst activation or maturation. These changes can result in the formation of new phases in the catalyst bulk [3, 4], or only in the surface layer [5].

According to the redox-model LLO should be inserted into the organic substrate molecule. This insertion has been proven by the ^{18}O-tracer experiments, e.g. for the molybdena catalysts [6] and for the scheelite ($Bi_{1-x/3}V_{1-x}Mo_xO_4$) structure catalysts [7].

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Hence, reaction networks of the partial oxidation must include a step of the Me–O bond breaking, before the lattice oxygen would be inserted into the substrate molecule. After the insertion, this bond must be regenerated. Therefore, the catalyst acts as an oxygen transmitter from the oxygen species causing full oxidation into LLO, and then into the organic molecule, but without cracking. Another problem is in which way the organic molecule is activated to remove oxygen from the oxide lattice.

Characterization of the redox-reactivity

The redox model briefly reminded above has caused many works on characterization of the redox-reactivity of the TMO catalysts. Among them there are studies of the catalysts reduction (usually by H_2) or reoxidation (usually by N_2O). According to the arbitrary chosen conditions a certain extent of the reduction is achieved, which is used as a measure of the LLO content. For example, a correlation was observed between the LLO content and the catalytic activity of MoO_3–$BiPO_4$ in toluene oxidation [8], and for the $(VO)_2P_2O_7$ catalysts in *n*-butane oxidation to maleic anhydride [9].

Applying the TPR method one can related catalytic properties to the onset temperature, and to the maximum rate temperature of the catalyst reduction. Such a correlation was observed for vanadia catalysts. Both these temperatures changed parallel to selectivity of methanol oxidation to formaldehyde, and *n*-heptanol to *n*-heptanal [10].

As the redox-model demands breaking of the Me–O bond, we should have got possibly detailed information about the strength of this bond. But, in spite of the numerous successes in case of the individual molecules, the quantum chemistry methods have not given concordant values of the Me–O bond strength in the TMO catalysts. So semiempirical and empirical methods are still used for this purpose.

For the last few years Ziołkowski has developed a semi-empirical method based on the bond length—bond strength—bond energy relation [11, 12]. In consequence, the crystallochemical model of the active sites in the TMO was formed [13]. Its helpfulness to characterize the various TMO catalysts will be perhaps confirmed in the future experimental works.

Spectroscopic methods seem to be adequate for measuring of the Me–O bond strength. But XPS gives us the binding energy of electrons from the internal orbitals. Although UPS can give the electron binding energies of the valence shell, the ultraviolet radiation generates a large charge on the oxide catalyst surface. This shifts the energy levels, what considerably hinders the spectra interpretation.

The IR spectroscopy is frequently used to identify the particular bonds, if only too high absorption does not exclude such measurements. The IR spectra however are rarely used as a measure of the bond strength. Lately, Johnson et al. [14] have determined a relation between the rate of selective oxidation of toluene to benzaldehyde and the frequency of the specific Me–O bonds.

The bond strength of the various adsorbed species (also the oxygen ones) is characterized by the activation energy of thermal desorption. But the bond strength of LLO may be characterized only by activation energy of the oxide decomposition [2]. A method, quite convenient for this purpose, is the temperature-programmed limited thermal decomposition (TPLTD), which has been used in our laboratory for various vanadium oxides [15] and for commercial catalysts [4].

The limited extent of thermal decomposition in TPLTD results in a simple kinetic equation. The specific decomposition velocity V (as in Fig. 1) (related to 1 g of the catalyst) does not depend on the decomposition extent, in consequence it fulfils the Arrhenius equation. Additionally, due to the construction of the apparatus this velocity is proportional to the oxygen pressure increase monitored by a mass spectrometer, in the outflow from the measuring cell [4, 15].

Characterization of the $Ag_xV_2Mo_yO_z$ samples

As a new example of the TPLTD application to the LLO characterization we present here the results concerning Ag-doping of V_2O_5–MoO_3.

The V_2O_5–MoO_3 catalysts are usually employed to the partial oxidation of aromates or alkenes to acid anhydrides or aldehydes. They are doped with various oxides to promote, or to modify these catalysts. The purpose of the present work is a preliminary characterization of the effect of Ag-doping on the V_2O_5–MoO_3 samples prepared by oxides melting.

Because the atomic ratio of V to Mo in the commercial catalysts is usually as 4 : 1, our samples had such a constant V : Mo ratio. Composition of all the samples of the series is described by formula $Ag_xV_2Mo_{0.506}O_z$, where $0 \leqslant x \leqslant 0.303$ and $5.759 \leqslant z \leqslant 5.911$.

The TPLTD experiments have shown two LLO forms, as two parts in the Arrhenius diagrams (Fig. 1). They are distinguished also in the Ag-free sample.

The weaker bound LLO is characterized by the constant activation energy of TPLTD, independently on the Ag-content (Fig. 2). The $Ag_xV_2Mo_yO_z$ samples have been studied in many respects, and generally, their particular properties vary with Ag-doping [16]. Only one exception has been noticed. The total reduction degree, i.e. the oxygen deficit in relation to the state of maximum oxidation numbers of all the metals in the system, is constant. One can say then that the bond strength of the

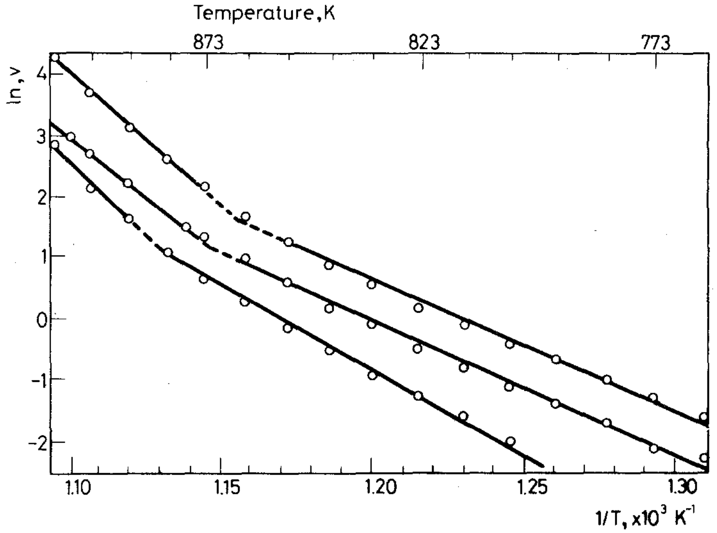

Fig. 1 Arrhenius plots of the TPLTD runs for the $Ag_{0.029}V_2Mo_{0.506}O_{5.744}$ samples, taken from the gauge scale. v is in arbitrary units. (In the regular experiments, the data were transmitted through an AC/DC converter to a MERA 400 computer [16]. The results of calculations were only printed)

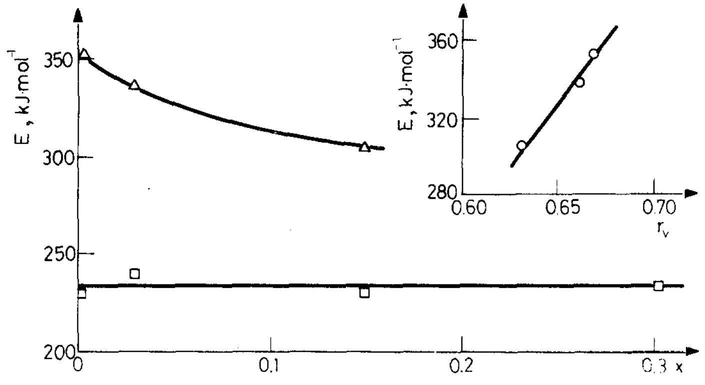

Fig. 2 Activation energy (E) of TPLTD as function of Ag-content x. Insert: linear correlation between E (for the stronger bound LLO form) and reduction degree (r_v)

weaker bound LLO correlates with the total reduction degree of the $Ag_xV_2Mo_yO_z$ samples.

The second, stronger bound from of LLO shows an activation energy greater than that of the first form. The difference is about 120 kJ mol^{-1} for the Ag-free sample. This difference diminishes with the Ag-doping (Fig. 2), because of weakening of the stronger bound LLO.

There is a linear correlation between the activation energy of the stronger bound LLO and the reduction degree arising from the oxygen vacancy concentration in the samples (Fig. 2, insert). It seems that the second form of oxygen ejection could have been related to removing of LLO from a second oxide phase, or to removing of a second type of oxygen atoms from the coordination polyhedra of the same phase.

The question needs further studies. At present, the first answer seems to be more reliable. X-ray analysis of the discussed samples have shown two phases: the Mo and Ag solution in V_2O_5, and the thermal decomposition of V_2O_{5-x} phase and V_2MoO_{8-r} phase was observed previously [15, 17].

References

1 A. Bielanski and J. Haber, Catalysis Rev.-Sci. Eng., 19 (1979) 1.

2 R. Dziembaj, J. Solid State Chem., 26 (1978) 167.

3 R. Dziembaj, ibid., 26 (1978) 159.

4 R. Dziembaj, S. Hodorowicz and G. Ciembroniewicz, J. Thermal Anal., 31 (1986) 761.

5 J. Haber, A. Kozłowska and R. Kozłowski, J. Catal., 102 (1986) 52.

6 G. W. Keulks and D. Krenzke, Proc. 6th Int. Congr. Catalysis, London 1976, Paper B–20.

7 W. Ueda, K. Asakawa, C.-L. Chen, Y. Mora-Oka and T. Ikawa, J. Catal., 101 (1986) 360 and 369.

8 J. M. D. Tascon, P. Grange and B. Delmon, J. Catal., 97 (1986) 299.

9 F. Cavani, G. Centi, F. Trifiro and G. Poli, J. Thermal Anal., 30 (1985) 1241.

10 J. Kijenski, A. Baiker, M. Glinski, P. Dollenmeier and A. Wokaun, J. Catal., 101 (1986) 1.

11 J. Ziołkowski, J. Solid State Chem., 57 (1985) 269.

12 J. Ziołkowski and L. Dziembaj, ibid., 57 (1985) 29.

13 J. Ziołkowski, J. Catal., 100 (1986) 45.

14 B. Jonson, R. Larsson and B. Rebenstorf, ibid., 102 (1986) 29.

15 R. Dziembaj, Proc. 4th Int. Symp. Heterog. Catalysis, Varna 1979, v. 1, p. 217.

16 R. Dziembaj and J. Surman, to be published.

17 R. Dziembaj and G. Ciembroniewicz, Proc. Conf. Solid State Chem., Cracov 1979, p. 51.

Zusammenfassung — Aus dem Konzept des labilen Gittersauerstoffs (LLO) als Konsequenz des Mars-Van Krevellen-Modells wird die Rolle der Oberflächen-Sauerstoff-Spezies hervorgehoben. Ein Überblick über die Methoden zur Charakterisierung der Me—O-Bindung wird unter besonderer Betonung der temperaturprogrammierten begrenzten thermischen Zersetzung (TPLTD) gegeben.

Eine Reihe $Ag_xV_2Mo_yO_z$ wurde mittels TPLTD charakterisiert, dabei konnten zwei Arten von LLO unterschieden werden. Die schwächere Form ist im Gegensatz zu der stärkeren unabhängig vom Silbergehalt. Die Aktivierungsenergie der TPLTD der stärker gebundenen LLO hängt linear von der Konzentration der Anionenfehlstellen ab.

Резюме — Понятие подвижного решеточного кислорода, вытекающее из модели Марса-Ван Кревеллена, было сопоставлено с поверхностными частицами кислорода. Приведено обозрение методов характеристики силы связи Me—O с особым ударением на температурно-программированную ограниченную термическую десорбцию. Этим методом был охарактеризован ряд соединений состава $Ag_xV_2Mo_yO_z$, для которых были разделены две формы подвижного решеточного кислорода. Более слабая форма его, по сравнению с более сильной формой, не зависит от легирования серебром. Энергия активации температурно-программированной граниченной темрической десорбции более сильно связанного подвижного решеточного кислорода являлась линейной функцией концентрации анионных вакансий.