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CANADA

EXCHANGE OF OXYGEN-18 WITH THE OXYGEN OF SOME CATALYSTS FOR SELECTIVE OXIDATION

PERMUTA DE OXIGÉNIO-18 COM O OXIGÉNIO DE ALGUNS CATALISADORES DE OXIDAÇÕES SELECTIVAS

The kinetics of exchange of gas-phase oxygen-18 with the oxygen of a series of molybdates of transistion metals, as well as with the oxygen of V_2O_5 and Nb_2O_5 has been studied. 51/1

It has been established that the surface and bulk oxygen exhibit energetically uniform behaviour with respect to the oxygen isotopic exchange. The rates of exchange of oxygen from the surface layer of the molybdates studied vary in the limits of one order. The activation energies vary also in very narrow limits (from 42 to 55 kcal.mol^{-1}). The correlation between the reactivity of oxygen in the compounds studied and their selectivity in catalytic oxidation reactions is discussed.

1. INTRODUCTION

It has been established during the last decade that a large series of selective oxidation reactions on oxide catalysts proceed through a reduction-oxidation mechanism (1).

Taking this experimental fact into account it can be assumed that the activity and selectivity of oxide catalysts will be influenced by the reactivity of oxygen in their surface layer.

The reactivity of surface oxygen in oxide catalysts can be successfully studied by the method of oxygen isotopic exchange. This method offers also a possibility to obtain information on the surface heterogeneity and the rate of oxygen self-diffusion in oxide catalysts.

The present communication contains results of a study of the isotopic exchange of molecular oxygen with the oxygen of V_2O_5, Nb_2O_5 and a series of metal molybdates, which are typical catalysts for selective oxidation.

2. EXPERIMENTAL

The metal molybdates were prepared by combined methods of precipitation and solid state reactions between molybdenum trioxide and the corresponding oxides of transition metals. Solutions of metal nitrates and ammonium paramolybdate were used. The suspension obtained during the precipitation was evaporated to dryness and the dry residue was calcined at 650 °C for no less 30 h. The high purity of the compounds obtained was confirmed by X-rays analysis, IR spectroscopy and chemical analysis.

The specific surface area of the specimens was measured and calculated by the BET method using krypton adsorption (−196 °C). Its value was 2,8 m^2/g for V_2O_5, 1,8 m^2/g for Nb_2O_5 and varied between 0,22 m^2/g and 7,70 m^2/g for the series of molybdates.

The oxygen isotopic mixture contained 20 % O_2^{18} and was prepared by dilution of oxygen-18 (99 % enrichment) with pure oxygen of natural isotopic composition.

The kinetic measurements were carried out by the static-circulation method using an all glass apparatus described previously (2). Analysis of the isotopic composition of the gaseous oxygen in the circulation loop was carried out periodically with a Hitachi-Perkin-Elmer model RMU double-focussing mass-spectrometer.

The measurements were performed mainly under the conditions of adsorption equilibrium. In order to remove adsorbed vapours and gases and to stabilize the content of oxygen in the surface layer of the sample, the latter were heat-treated for 4 hours in vacuum (10^{-5} Torr) and then at a pressure of 10 Torr for 2 h in pure oxygen with a natural isotopic composition. Experiments were mostly carried out at 10 Torr while for the estimation of the reaction order the pressure was varried between 5 and 50 Torr.

3. RESULTS AND DISCUSSION

The rate of exchange was calculated from the equation:

$$R = \frac{-\mathrm{Ln}(1-F).N_s}{S.(1+\lambda).t}$$

where F is the extent to which equilibrium has been approached and is defined as $F = (Co\text{-}C)/(Co\text{-}C_\infty)$. Co is the initial concentration of O^{18} (at. %) in the gaseous phase, C is the concentration of O^{18} in the time t and C is the equilibrium concentration of O^{18} defined on the basis of a material balance. Thus $C_\infty = (Co + 0{,}2)/(1 + \lambda)$, where 0,2 is the natural content of O^{18} (at. %); $\lambda = Ns/Ng$, where Ns is the number of the exchangeable oxygen atoms in the oxide sample and Ng is the number of the exchangeable oxygen atoms in the gaseous phase. S is the total surface area of the sample (cm^2) and R is the exchange rate per unit surface area in molecules/cm^2.sec.

The fraction X of the surface oxygen atoms attaining the isotopic composition of the gaseous phase was calculated from the experimental data according to the equation:

$$X = \frac{Co - C}{\lambda'(C - 0{,}2)}$$

where λ = Nsurf./Ng is the ratio of the quantity of oxygen in the surface layer of the oxide and in the gaseous phase and 0,2 the natural concentration of O^{18}.

The applicability of eq. 1 to the calculation of the exchange rates is demonstrated in fig. 1, in which the dependence of Lg(I–F) on the duration of exchange is plotted for several experiments. It was found that the equation quite satisfactorily described the experimental results. The validity of eq. 1 shows that the oxygen in the investigated compounds behaves as energetically uniform with respect to the exchange.

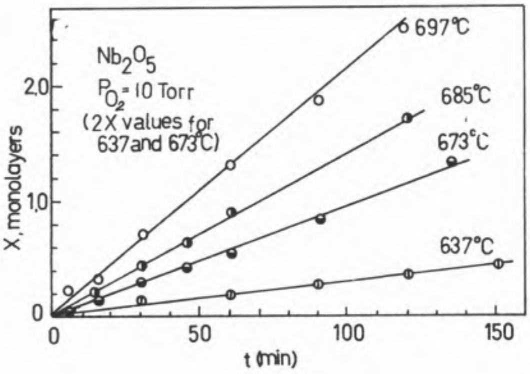

Fig. 1

The established linear character of the dependence Lg(I–F) = f(t) to degrees of exchange corresponding to scores of monolayers indicates a high rate of oxygen selfdiffusion in the compounds under investigation.

Fig. 2 shows a typical dependence of the fraction of surface oxygen attaining the isotopic composition of the gaseous phase X, on the duration of the exchange.

In table 1 the experimental data on the activation energy of exchange are given.

A comparison of the specific rates of exchange at 600°C is given in fig. 3.

As was established previously (3,4) in the case of transition metal oxides, the activation energies of exchange vary from 16 to 60 kcal.mol^{-1}, whereas with the corresponding molybdates the changes are in the limits of 14 kcal.mol^{-1}. When taking into account the lower thermal stability of the copper (II) molybdate, the range of the activation energy of exchange with the molybdates under consideration is reduced to 7 kcal.mol.

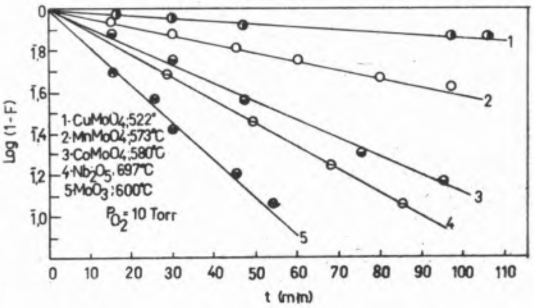

Fig. 2

Table 1

Activation energies of oxygen isotopic exchange, kcal.mol^{-1}

Catalysts	Temperature intervals	Ea kcal.mol^{-1}
$CuMoO_4$	500 – 600 °C	42
$Fe_2(MoO_4)_3$	520 – 600	52
$MnMoO_4$	540 – 610	55
$Cr_2(MoO_4)_3$	540 – 610	54
$ZnMoO_4$	550 – 600	48
$CoMoO_4$	550 – 600	54
MoO_3	550 – 620	58
V_2O_5	350 – 420	52
Nb_2O_5	620 – 700	61

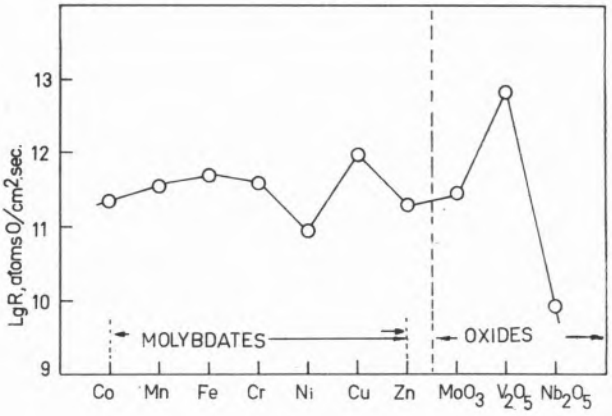

Fig. 3

The differences observed when comparing the specific rates of exchange under isothermal conditions (600 °C, P_{O_2} = 10 Torr) are even more pronounced. While in the case of simple oxides the above parameter varies within the range of 5 orders of magnitude, with the corresponding molybdates the changes are in the narrow limits of I order of magnitude.

Another important peculiarity should also be mentioned. In the case of some simple oxides of transistion metals, the surface oxygen behaves as strongly inhomogeneous with respect to the oxygen isotopic exchange and can be quite different in mobility and reactivity from lattice oxygen. This difference is practically not observed in the case of the corresponding metal molybdates. A measurable difference between their surface and bulk oxygen has not been observed.

The reactivity of oxygen in the surface layer of the molybdates studied is very close to the reactivity of oxygen in the surface layer of MoO_3. The influence of the bivalent or trivalent cations of the second metal in these compounds is relatively small. Moreover, a more general tendency was observed: the reactivity of oxygen in the complex oxide catalysts, which could be considered as consisting of two oxides, usually approaches the reactivity of oxygen in the oxide forming the anionic component. This reactivity is close to that of oxygen in MoO_3 in the case of molybdates and to that of V_2O_5 in the case of vanadates, etc.

It is interesting to note that the reactivity of oxygen in V_2O_5 and Nb_2O_5 is close to the reactivity of oxygen in the molybdates studied. The activation energy of exchange is in the range of the activation energies found for the molybdates studied. Besides, the considered peculiarities of the molybdates studied remain valid also for these two oxides. Moreover, it was found that with these two groups of catalysts for selective oxidation one and the same mechanism of exchange is predominant. The main stage of this mechanism is the exchange of two atoms from the gaseous phase with two oxygen atoms from the surface of the catalysts (6).

According the current conceptions, there is a correlation between the rate and the activation energy of exchange of molecular oxygen with the oxygen of oxides and salts and their activity and selectivity in a large group of reactions proceeding according to a redox mechanism (1–4).

As was shown in a previous paper (3) and confirmed in a series of other works, in the case of weakly bound and highly reactive oxygen in the surface layers of the catalysts, the oxidation proceeds mainly to products of complete oxidation. With lower reactivity of oxygen in the surface layer, a selective oxidation with a appropriate rate is more probable.

The results of the present study are in good agreement with this conception. Vanadium pentoxide and niobium pentoxide whose surface oxygen has relatively low reactivity are basic components of selective catalysts for a large series of reactions of selective oxidation of hydrocarbons and alcohols. Ferric, nickel and manganese molybdates are highly selective catalysts in the oxidation of methanol to formaldehyde (5).

The present study shows that for a selective oxidation the existence of surface oxygen with a relatively low reactivity is a necessary condition. At the same time the selectivity should also depend on the specific activation of the molecule to be oxidized.

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RESUMO

Estudou-se a cinética da permuta de oxigénio-18 gasoso com o oxigénio de uma série de molibdatos de metais de transição, assim como com o oxigénio do V_2O_5 e Nb_2O_5.

Verificou-se que o oxigénio da superfície e da massa tem um comportamento energético uniforme em relação à permuta isotópica de oxigénio. As velocidades de permuta do oxigénio da camada superficial dos molibdatos estudados variam nos limites de uma ordem de grandeza. As energias de actividade também variam dentro de limites muito apertados (de 42 a 55 kcal.mole^{-1}).

É discutida a correlação entre a reactividade do oxigénio nos compostos estudados e a sua selectividade nas reacções de oxidação catalítica.

DISCUSSION

P. FORZATTI : In the IR spectra you showed it appears from the presence of the vibrational mode at 990 cm^{-1} ($\upsilon_{Mo = O}$ in MoO_3) that small quantities of MoO_3 are still present in the molybdates you studied. Do you think that these impurities could have affected your results ?

D. G. KLISSURSKI : The shown spectra correspond to freshly synthetized preparations. They were additionally calcined until the disappearance of eventual MoO_3 impurities.

I. MATSUURA : A question are a point of detail related crystal structure of molybdates to the oxygen exchange reaction.

As you know $MnMoO_4$ has two tetrahedral coordinated oxygen to Mo that is very stable. However $NiMoO_4$ has an octahedral coordinated oxygen to Mo that is also stable lower than 660 °C.

Your data did not give any different effects for different coordination of Mo in the molybdates. How is it possible to explain that the relatively same rate of oxygen exchange to MoO_3 ?

D. G. KLISSURSKI : There is a difference between the reactivities of oxygen in the surface layer of molybdates of first transition row metals.

As was pointed out, however, the variation in the rate of oxygen exchange with this group of molybdates at 600 °C is within very narrow limits (less than 10 times).