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Anomalously Low Bond Energy of Surface Oxygen on FeZSM-5 Zeolite

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Calorimetric measurements have shown that surface oxygen resulting from N_2O decomposition on FeZSM has an anomalously low bond energy, which accounts for some peculiar properties of this oxygen, including its high reactivity.

There are two temperature regions of N_2O decomposition on iron-containing zeolite FeZSM-5.[1,2] Below 300 °C decomposition proceeds according to reaction (1)

$$N_2O + (\ ) \rightarrow (O) + N_2 \qquad (1)$$

with fixation of oxygen atoms on the active centres of the surface. When all centres are occupied, the reaction stops. In the high-temperature region (above 300 °C) N_2O decomposition occurs as a 'normal' catalytic process with evolution of stoichiometric amounts of dinitrogen and dioxygen according to reaction (2).

$$N_2O \rightarrow N_2 + 1/2\ O_2 \qquad (2)$$

The surface oxygen (O), formed by reaction (1), exhibits some unusual properties: (*i*) it cannot be produced by O_2 adsorption since dioxygen does not interact with the active centres of FeZSM-5 even at 550 °C; (*ii*) it shows a remarkably high reactivity. At room temperature it is involved in both O_2 isotopic exchange and oxidation of CO and CH_4.[2] According to a generally accepted idea, the high reactivity of surface oxygen is due to the low energy of its bond to the surface.[3] The heat of adsorption of dioxygen, q_{O_2}, corresponding to reaction (3),

$$O_2 + 2(\ ) \rightarrow 2(O) \qquad (3)$$

is usually accepted as a characteristic of the surface bond energy. Values of q_{O_2} measured for metal oxides vary within wide limits, from 60 kcal/mol O_2 for TiO_2 to 16 kcal/mol O_2 for Co_3O_4,† which is known to have the most active surface oxygen. From this point of view one can expect a low value of q_{O_2} for FeZSM-5. Theoretically it might even be negative since the source of oxygen delivery to the surface is of an endothermic nature, $\Delta_f H°(N_2O) = +19.5$ kcal mol^{-1}.[4]

In order to measure the bond energy of the surface oxygen on FeZSM-5 zeolite we used a sample with 0.5 wt % Fe_2O_3 studied previously[2] and designated as Fe-0.5. This sample has a sufficiently large number of active centres (8.4×10^{18} g^{-1}) to ensure reliable calorimetric measurements. Since reaction (3) does not take place directly on Fe-0.5, we measured the heats of reactions (1) and (2), q_1 and q_2 respectively, combination of which gives the value of q_{O_2}.

Experiments were carried out in a pulse catalytic system with a reactor placed in a Tian–Calvet microcalorimeter.[5] Pulses of reaction mixture (7.5% N_2O in He) were periodically introduced into a helium stream passing through the reactor containing the Fe-0.5 catalyst. The system permits both heat evolution measurements and the determination of the quantity of N_2O decomposed. The value of q_1 was measured at 200–275 °C and that of q_2 at 510 °C. Before each experiment for measurements of q_1 the sample was pretreated in helium at 510 °C for 1 h to ensure complete desorption of the surface oxygen.

Fig. 1 illustrates the dependence of q_1 on surface oxygen loading, θ, measured during experiments at 275, 242, 205 and 200 °C. Each experiment consists of several measurements carried out during 3–4 successive pulses. One can see that the mean q_1 value [curve (*a*)] decreases with increasing θ, but within a reasonable data scatter it does not depend on temperature. Line (*b*) in Fig. 1 shows a value of q_2 18.5 (± 0.5) kcal/mol N_2O, which is in good agreement with the enthalpy of formation of N_2O. The mean value of the heat of adsorption of oxygen at different θ, calculated as $q_{O_2} = 2(q_1 - q_2)$, is presented in Table 1. q_{O_2} varies from 6 (± 3.5) to 1.0 (± 3.5) kcal/mol O_2 when the oxygen loading approaches 50% of its maximum level. In any case these values correspond to an anomalously low bond energy for atomically adsorbed oxygen. This accounts for the peculiar properties of oxygen on FeZSM-5 noted above, its remarkable reactivity and the impossibility of its formation from O_2.

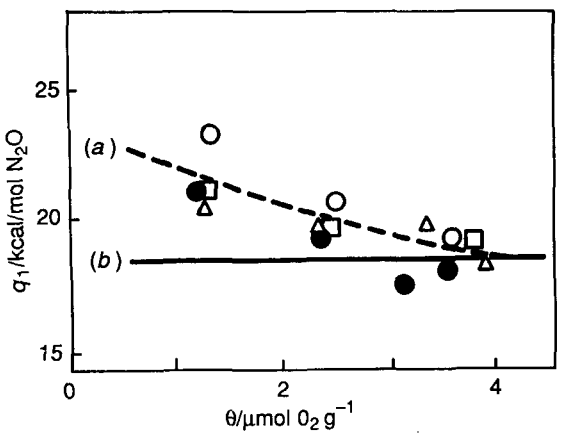

Fig. 1 Heat of reaction for N_2O decomposition on Fe-0.5: (*a*) decomposition with oxygen fixation [reaction (1)] at temperatures 275 (□), 242 (○), 205 (△), and 200 °C (●); (*b*) decomposition with oxygen evolution [reaction (2)]

In order to explain the fairly high thermal stability (up to 300 °C) of such weakly bound oxygen it is possible to assume that decomposition of N_2O and fixation of oxygen atoms occur on single isolated active centres separated from one another by high energy barriers presenting surface diffusion. This is favoured by a low surface density of active centres (about 3×10^{16} centres m^{-2} in the case of Fe-0.5). This assumption is consistent with the fact that surface oxygen (O) cannot be formed from NO, although the thermodynamic properties of NO and N_2O are very similar.[4] The mechanism of NO decomposition is more complicated.[6] Unlike reaction (1) the NO

Table 1 Heat adsorption of oxygen, q_{O_2}, on Fe-0.5

θ/μmol O_2 g^{-1}	q_{O_2}/kcal/mol O_2 (± 3.5)
1.3	6.0
2.0	4.0
2.5	2.5
3.0	1.5
3.5	1.0
4.0	1.0

† 1 cal = 4.184 J.

dissociation step cannot be realized at a single active centre which is probably why decomposition of NO does not take place on Fe-0.5 even at 550 °C.[2]

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