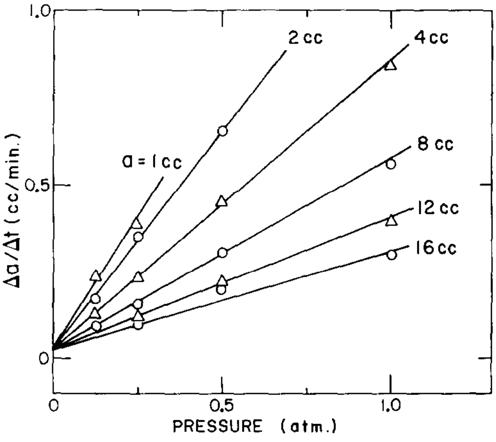

FIG. 4. Plot of $\Delta a/\Delta t$ against pressure for hydrogen on chromia (*2*). Catalyst weight 16 g, temperature 457°K.

and Taylor on the adsorption of hydrogen on chromia gel (*2*), in which again good linearity against pressure is seen. Although the intercepts are slightly positive, they are close to zero, suggesting that the adsorption is so strong that the desorption rate is negligible. The plot of log r thus obtained against the adsorbed amount gave two straight lines: one from 1 to 4 cc with a large slope; the other from 4 to 16 cc with a smaller slope. Taylor and Thon also indicated that Burwell's results fitted the Elvoich equation up to 2 cc (*3*).

As described above, the present treatment is not only useful for obtaining net rates of adsorption and desorption, but also is applicable to heterogeneous surfaces, since $\Delta a/\Delta t$ is taken at the same surface coverage. Furthermore, when r_a and r_d are separately obtained as functions of p and a [the detailed forms of $g(\theta)$ and $h(\theta)$ are not necessary], the isotherm can be predicted. It is also clear that the method is not limited to adsorption, but, in principle, is applicable to general reactions if suitable data are available.

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Y. AMENOMIYA

Division of Applied Chemistry
National Research Council
Ottawa 7, Canada

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NOTES

Classification of Oxidation Catalysts According to the Type of Metal–Oxygen Bond*

INTRODUCTION

In recent years, many correlations have been made between the strength of the metal–oxygen bond of oxidation catalysts and their activity in the oxidation of several types of molecules (*1–4*).

It is known from organic and inorganic chemistry that the reactivity of a bond not only depends on its strength but also on its type.

In a previous article (*5*) we drew attention to the relationship existing between the activity in NH_3 and C_3H_6 oxidation of a series of molybdates studied by us and the presence of a metal–oxygen bond having double-bond character. No hypotheses were put forward on how such a metal–oxygen

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bond might participate in the oxidation reactions. However, the existence of other oxidation catalysts without a metal–oxygen bond of this type suggested that, if oxygen participated directly, these catalysts should possess different mechanisms of oxidation. For this purpose, we have classified several oxides and mixed oxides, which are oxidizing catalysts at a rather low temperature ($T < 350°C$) according to the nature of the metal–oxygen bond.

Data

Table 1 reports a series of oxides and mixed oxides that are catalysts of the oxidation of propylene, ammonia, and methanol at $T < 350°C$. Catalysts that are active in the oxidation reactions at higher temperatures, like TiO_2, ZnO, Sb_2O_3, WO_3, have been excluded. We have indicated whether each catalyst is active in the oxidation of CO and in the isotopic homomolecular exchange of oxygen. The same table also reports the types of products obtained in the oxidation of NH_3 and the selectivity in CH_2O and in acrolein, respectively, for the oxidation of methanol and propylene, as well as the energy of activation of the isotopic homomolecular exchange of O_2 and whether these catalysts exhibit a metal–oxygen bond having double-bond character.

We deduced that these catalysts contain a metal–oxygen bond having double-bond character from the presence of a band in the region near 1000–900 cm^{-1} in the infrared spectra (*6*).

As shown in this table, the oxidation catalysts may be grouped into two classes exhibiting similar catalytic behavior.

1st Class. Oxidation catalysts that do not possess a metal–oxygen bond having a double-bond character: NiO, Co_3O_4, CuO, Cr_2O_3, MnO_2, Fe_2O_3, $CdMoO_4$, SnO-Sb_2O_3 belong to this class. These catalysts are active in the oxidation of CO and are generally very active in the isotopic homomolecular exchange of O_2 (*7*). In the oxidation of methanol, they essentially give CO_2 (*8*). In the oxidation of NH_3—except for SnO-Sb_2O_3 (*8*)—they give high amounts of N_2O (*9*) and in the oxidation of propylene—except for SnO–Sb_2O_3—they give only CO_2 (*8, 10*).

2nd Class. Oxidation catalysts that possess a metal–oxygen bond with double-bond character: V_2O_5,MoO_3 and Fe, Bi, Co, Ni, and Mn molybdates belong to this class. These catalysts are not active or their activity is very low in the oxidation of CO and in the isotopic homomolecular exchange of oxygen, at the temperatures at which they are active in the oxidation of propylene, ammonia, and methanol. In the oxidation of ammonia, they give only N_2 (*9–11*), whereas in the oxidation of methanol at $T < 350°C$, they can reach—except for V_2O_5—a selectivity in CH_2O higher than 80% (*7, 12*). In the oxidation of propylene to acrolein, some of the catalysts of this class are selective, others are not (*8, 11*).

Discussion

As can be deduced from Table 1, a classification of oxidation catalysts according to the presence or not of a metal–oxygen double bond can help us to predict the catalytic behavior with regard to the reactions of oxidation of simple molecules, i.e., CO, NH_3, CH_3OH.

The catalysts of the first class, owing to their higher activity in the oxidation of CO and to the type of products that they give in the oxidation of ammonia and methanol, can be called more properly oxidation catalysts.

The catalysts of the second class, owing to their low activity in the oxidation of CO and to the high yield of CH_2O that they give in the oxidation of CH_3OH, can be denominated dehydrogenation catalysts.

By considering the high rate of isotopic homomolecular exchange of oxygen and the lower energy of activation of this reaction, the oxidizing power of the catalysts of the first class can be connected with their ability to adsorb oxygen from the gas phase in the activated form. Activated oxygen can initiate oxidation by reacting with propylene either in the gas phase or in an adsorbed form.

In our opinion, the dehydrogenating power of the catalysts of the second class is

TABLE 1

PROPERTIES OF OXIDIZING CATALYSTS

	Oxidation of COat $T < 350°$	Selectivity in oxidation of CH_3OH^a at $T < 350°C$	Product obtained in the oxidation of NH_3	Selectivity in oxidation of $C_3H_6{}^b$ at $T < 350°C$	Rate of homomolecular exchange of oxygen at 300°C[c]	Energy of activ. of homomol. isotopic exchange of oxygen (kcal/mole)	Presence of a band at 1025–900 cm^{-1}
MnO_2	Active (*7*)	$\simeq 10$ (*7*)	N_2O–N_2 (*9*)	<5 (*10*)	2.1×10^{12} (*7*)	22 (*7*)	Not
Fe_2O_3	Active (*7*)	$\simeq 10$ (*7*)	N_2O–N_2 (*9*)	<5 (*10*)	9.4×10^{9} (*7*)	33 (*7*)	Not
Co_3O_4	Active (*7*)	$\simeq 10$ (*7*)	N_2O–N_2 (*9*)	<5 (*10*)	3.2×10^{13} (*7*)	16 (*7*)	Not
NiO	Active (*7*)	$\simeq 10$ (*7*)	N_2O–N_2 (*9*)	<5 (*10*)	6.7×10^{11} (*7*)	24 (*7*)	Not
CuO	Active (*7*)	10 (*7*)	N_2O–N_2 (*9*)	<5 (*10*)	7×10^{11} (*7*)	26 (*7*)	Not
Cr_2O_3	Low activity (*7*)	15 (*7*)	N_2O–N_2 (*9*)	<5 (*10*)	6.1×10^{7} (*7*)	42^d	Not
$CdMoO_4$	Active (*8*)	<10 (*8*)	N_2O–N_2 (*8*)	<5 (*8*)	—	—	Not
SnO–Sb_2O_5	Active (*8*)	<10 (*8*)	—	70 (*8*)	—	—	Not
V_2O_5	Low activity (*6*)	$\simeq 50$ (*7*)	N_2–N_2O traces (*9*)	$\simeq 34$ (*8*)	1×10^{7} (*7*)	46 (*7*)	Yes
MoO_3	Inactive (*8*)	(*7*)	N_2 (*9*)	$\simeq 70$ (*11*)	2.6×10^{3} (*7*)	69 (*7*)	Yes
Fe molybdate	Inactive (*8*)	(*12*)	N_2 (*11*)	<5 (*11*)	Comp. with MoO_3 (*1*)	—	Yes
Co molybdate	Inactive (*8*)	>80 (*12*)	N_2 (*11*)	<5 (*11*)	—	—	Yes
Ni molybdate	Inactive (*8*)	(*12*)	N_2 (*11*)	<5 (*11*)	—	—	Yes
Mn molybdate	Inactive (*8*)	(*12*)	N_2 (*11*)	<5 (*11*)	—	—	Yes
Bi molybdate	Inactive (*8*)	(*12*)	N_2 (*11*)	$\simeq 80$ (*11*)	—	—	Yes

[a] $(C_{CH_2O}/C_{CH_3OH\,reacted}) \times 100$

[b] $(C_{acrol.}/C_{C_3H_6\,reacted}) \times 100.$

[c] torr mole/cm² sec.

[d] In an oxidizing atmosphere Cr_2O_3 can be oxidized to CrO_3 that has a Cr–O double bond (*6*). This is the reason why we think that Cr_2O_3 possesses a high-energy activation and a low rate of isotopic homomolecular exchange of O_2 (*7*), this behavior is characteristic of the second class of catalysts.

directly connected with the metal–oxygen double bond. In order to describe how this bond can influence the dehydrogenation of molecules present on the surface of the catalysts, we refer to the structure of the crystals of molybdenum oxide.

Kihlborg (*13*) reports that by reduction of MoO_3 under vacuum at $T < 550°C$ some nonstoichiometric oxide having a crystal structure consisting of octahedral and of pentagonal bipyramid were obtained. The pentagonal bipyramid that forms from the opening of the metal–oxygen double bond leaves a free valence on molybdenum, thus increasing its possible coordination.

We think that the mechanism of adsorption or of reduction of the catalysts by the molecule in the gas phase is similar to that of vacuum reduction of MoO_3. An H atom (ion or radical withdrawn from a molecule present on its surface, i.e., propylene, ammonia, methanol) can be added to a metal–oxygen double bond of the catalysts. The opening of the double bond leaves a free valence on the metal, and it may be used in a bond with the dehydrogenated molecule. This free valence, in the case of the oxidation of propylene after a possible adsorption as a π-olefin complex, can be used to give an allyl complex.

The molecule activated in this way may be subjected to further reactions.

As to the mechanism just pointed out for oxidation by dehydrogenation catalysts, the first stage must be the reaction of the molecule to be oxidized with the oxygen of the catalysts. This is typical for an oxidation mechanism of the oxyreductive type. This oxyreductive mechanism has generally been proposed for catalysts containing a metal–oxygen bond having double-bond character: V_2O_5 (*14*), BiO_3-MoO_3 (*15*), Fe_2O_3-MoO_3 (*16*).

In addition, Klier and coworkers (*17*) report that in isotopic exchange reactions between gaseous oxygen and the oxygen of the catalysts, only V_2O_5, MoO_3, and WO_3 may exchange the lattice oxygen; on the contrary NiO and Co_3O_4, which belong to the first class, just exchange the surface oxygen. Therefore, it may be assumed that the mechanism of the catalysts of the second class more probably is of the oxyreductive type and that of the catalysts of the first class is of the Langmuir or Rideal type. We feel that this last assumption must be limited to the oxidation of simple molecules or to reactions of oxidation that preserve the number of carbon atoms.

It can hardly be stated that only a redox mechanism is involved for catalysts of the second class that in the oxidation of propylene give essentially CO_2. Some intermediate oxidized compounds of propylene can be so reactive that they adsorb oxygen from the gas phase.

The failure of every correlation between the type of metal–oxygen bond and selectivity in the oxidation of propylene supports the limitation just pointed out.

Some exceptions are also found in the oxidation of propylene with catalysts of the 1st class. In fact, SnO-Sb_2O_3 exhibits a high selectivity in the oxidation of propylene to acrolein.

Therefore, for the oxidation of complex molecules, other parameters can determine the catalytic behavior of oxide and of mixed oxides.

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Ferruccio Trifirò
Italo Pasquon

Instituto di Chimica
Industriale del Politecnico,
Milano, Italia

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