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Metal–Insulator Transition and a Selectivity of a Catalytic Reaction: Propylene over Na_xWO_3

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Catalytic reactions of propylene have been investigated over unsupported Na_xWO_3 to see how the metal–insulator transition of the catalyst affects the selectivity toward dimerization or metathesis. It was found that dimerization was dominant over an insulating solid and metathesis was over a conducting one. Especially for $Na_{0.25}WO_3$, reduction of the catalyst altered the type of the reaction completely from dimerization to metathesis at 473 K together with the conductivity transition. A contribution of conduction electrons was discussed both from static and dynamical points of view.

INTRODUCTION

It was found that dimerization was dominant over insulating WO_3 and metathesis was over metallic ReO_3 at 473 K (*1, 2*). The latter is an isoelectronic analog of $NaWO_3$. WO_3 and $NaWO_3$ are end members of Na_xWO_3 and it has insulating properties when $x \lesssim 0.25$ and metallic electrical conductivity when $x \gtrsim 0.25$ (*3*). Na atom supplies an electron to a WO_3 lattice. Thus it will be an interesting problem to see how the catalytic reaction will change from dimerization to metathesis over unsupported Na_xWO_3 when x is increased from zero to one.

If dimerization and metathesis occur through a two-molecule collision, the substantial difference between the two will be in the breaking of the double bond between carbon atoms. However, metathesis is believed to occur via metallacyclobutane especially over homogeneous and supported heterogeneous catalysts (*4*). If the model is also real over unsupported catalysts, the substantial difference between the two reactions would be in the strength of the metal–carbene bond assuming that the two reactions occur on the same active points.

In this work, details of a mechanism of metathesis will not be considered but efforts will be made to find out how the metal–insulator transition affects the selectivity toward dimerization or metathesis over unsupported Na_xWO_3.

EXPERIMENTAL METHODS

Na_xWO_3 was prepared from 99.9 wt% WO_3, 99.9 wt% WO_2, and Na_2WO_4. Starting materials were mixed and pressed into tablets and heated under a vacuum of 10^{-4} Torr (1 Torr = 133.3 N m^{-2}) at 1223 K for 13 h. Then they were ground into powders and mixed again. After pressed into tablets again, they were heated under the same conditions as before. A bar was cut from a tablet for an electrical resistivity measurement. That was done with a usual four-probe method with silver-painted electrodes.

The tablets were ground in air for the use of catalysis experiments and they will be called as-prepared catalysts hereafter. X-Ray diffraction patterns were taken to certify the formation of Na_xWO_3. x is the nominal value and a chemical analysis was not done. The BET areas were as small as 3 m^2/g and since the errors were large, experimental results were not normalized with the surface area.

Chemical reactions were done in a closed reactor and experimental details were de-

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TABLE 1

Some Examples of Products over Na_xWO_3

	x	wt (g)	BET area (m^2/g)	$C_2H_4 + C_2H_6$ ($\times 10^{-5}$)	C_3H_8 ($\times 10^{-5}$)	$1\text{-}C_4H_8$ + iso-C_4H_8 ($\times 10^{-5}$)	$2\text{-}C_4H_8$ ($\times 10^{-5}$)	C_5H_{10} ($\times 10^{-5}$)	C_6H_{12} ($\times 10^{-5}$)	Reaction temp. (K)
a	0	4.89	3.6 ± 1	40	440	430	250	1900	2400	473 ± 1
b	0	4.00	2.6	310	170	14	260	19	270	423
c	0.08	4.90	2.9	220	2930	900	740	3200	2700	473
d	0.08	4.78	2.9	5		2	4	8	79	473
e	0.1	4.86	2.0	12	110	1	9	3	160	423
f	0.1	4.86	2.0	78	53	0	71	0	26	423
g	0.1	4.02	2.0	570	180	53	390	83	360	423
h	0.25	4.98	3.2	1	240	3	1	7	350	473
i	0.25	4.98	3.2	74	104	0	72	0	0	423
j	0	3.01	2.6			5	34	0	0	473
k	B			34	0	15	3	21	31	573
l				17	0	0	0	0	0	

Note. Concentrations were expressed relative to that of propylene except j. Errors were ±10%. Reaction period was 20 min except c, d, and k. Reduction was done with propylene except g. (a) As-prepared. (b) Reduced at 773 K for 20 min. (c) As-prepared, reaction period 12 h. (d) Oxidized in air at 673 K for 3 h, reaction period 12 h. (e) Reduced at 473 K for 80 min. (f) Reduced at 573 K for 80 min. (g) Reduced with hydrogen at 823 K for 60 min. (h) As-prepared. (i) Reduced at 673 K for 80 min. (j) Ethylene was reacted over WO_3 at 473 K for 20 min. (k) Propylene was reacted at 573 K for 12 h without a catalyst. (l) Impurity levels in initial propylene.

scribed elsewhere (*2*). Catalysts were usually about 4 g. Degassing of the catalysts were done at 473 K for 60 min under the vacuum of 2×10^{-4} Torr when the reaction temperatures were lower than 423 K and at the reaction temperature when it was higher than 473 K. As-prepared catalysts were sometimes annealed in air at 673 K for 3 h to eliminate oxygen vacancies. The reactions were done in the successive way of Ref. (*2*).

RESULTS

Table 1 shows some examples of the products of 20-min-reactions for various catalysts. Concentrations were expressed relative to that of propylene and were not normalized to a unit area. Isobutene and 1-butene were not separated exactly and their sums are shown in the table (the same for ethylene and ethane).

As seen from Table 1, the results are classified into two groups. In one group, the main products are hexenes, pentenes, (iso + 1)-butenes, propane, ethane, and ethylene. Hexenes were produced mostly. The main component of hexenes was 2-methyl-2-pentene suggesting that they are not the products of the reaction in which lattice oxygen takes a part (*5*, *6*). In the other group, the main products are ethylene and 2-butenes and they are the products of metathesis. The former group will be nominated as D group (dimerization) and the latter as M group (metathesis). It must be noted that these two groups cannot be specified only by the x value of Na_xWO_3 but reduction of catalysts affected the results for the most part. For the D group, not only hexenes but also pentenes and other olefins were produced as shown in Table 1. Those might have been the products of molecular collisions of propylene because they were produced even without a catalyst as shown in Table 1-k. Moreover 2-butenes were produced from ethylene over WO_3 indicating that dimerization really occurred as shown in Table 1-j. Thus hexenes will be treated as the main products of that process and pen-

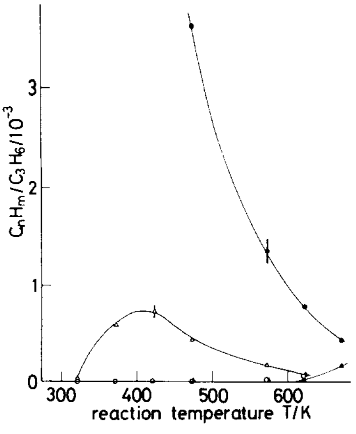

FIG. 1. Products dependencies in relation to the reaction temperature over $Na_{0.25}WO_3$. Reaction period was 20 min. Solid circles and triangles stand for hexenes and 2-butenes, respectively, in the increasing temperature over as-prepared catalyst. Open circles and triangles stand for hexenes and 2-butenes, respectively, in the increasing temperature over the catalyst which had been reduced with propylene at 673 K for 80 min. Through the experiment, the same catalyst was used successively (*2*).

tenes and other olefins will be neglected hereafter for D group.

Figure 1 shows the most drastic effect of the reduction on the reaction over $Na_{0.25}WO_3$ which is at the boundary of the metal–insulator transition. Solid symbols show the results in the increasing temperature over as-prepared catalyst which was not reduced intentionally prior to the reaction. The catalyst did not show a metallic conductivity before the reaction. After the reaction at 673 K for 80 min, it was cooled to 323 K and the reactions were repeated in the increasing temperature as before. The reaction period was 20 min. In the second run, the catalyst can be considered to have been reduced prior to the reactions because it showed a very high electrical conductivity. Moreover an X-ray diffraction pattern showed a change in the crystalline structure. Usually a metal–insulator transition accompanies a structure change. Open symbols in Fig. 1 show the results over thus reduced catalyst. As seen from the figure, hexenes disappeared at lower temperatures whereas 2-butenes were produced largely compared with the former results. Thus the type of reaction changed drastically from D to M after the reduction.

The resistivity of a sintered $Na_{0.25}WO_3$ became very low with reduction as shown in Fig. 2. The reduction was done with propylene at 673 K for 90 min. The resistivity change of the sintered bar might not be larger than that of the powdered catalyst since the powders were reduced at 673 K for 80 min. In Fig. 2, similar results for bars of $x = 0$ (rectangles) and $x = 0.4$ (triangles) are also shown. Solid and open symbols stand for as-prepared and reduced catalysts, respectively. Reductions were done under the same conditions as those for $Na_{0.25}WO_3$.

Figure 3 shows the reduction effect on the catalytic reactions over WO_3 where solid symbols stand for reduction with propylene at 623 K for 20 min and open symbols at 773 K for 20 min. After the reduction at 773 K the WO_3 turned blue. As seen from Fig. 3, reduction made metathesis more active and suppressed dimerization as before.

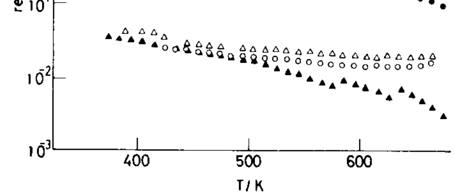

FIG. 2. Resistivities of sintered oxides under vacuum were plotted against measuring temperature. Rectangles stand for WO_3, circles for $Na_{0.25}WO_3$, and triangles for $Na_{0.4}WO_3$. Solid symbols stand for as-prepared oxides in the increasing temperature and open symbols for reduced oxides in the decreasing temperature. Reductions were done with propylene at 673 K for 90 min, respectively. Some discontinuities in the curves were due to introduction of propylene of 1 atm for a short while at those temperatures.

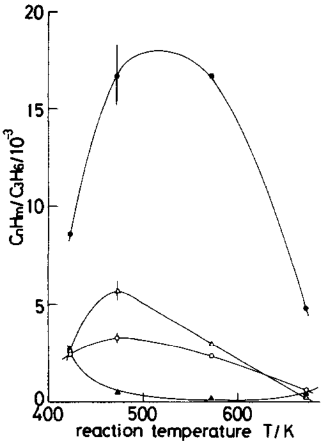

FIG. 3. Product dependencies in relation to reaction temperature over WO_3. Reaction period was 20 min. Circles and triangles stand for hexenes and 2-butenes, respectively, in the increasing temperature. Solid symbols are for WO_3 reduced with propylene at 623 K for 20 min and open symbols are for WO_3 reduced with propylene at 773 K for 20 min.

The type of reaction may be represented with a parameter y which is defined as

$$y = (\text{2-butenes})/(\text{2-butenes} + \text{hexenes}), \tag{1}$$

where quantities are concentrations. Thus it is M type when y is equal to one and D type when y is zero. Figure 4 shows how this y changed as the reaction temperature was raised for various catalysts. y became larger when a catalyst was reduced. For instance, y of WO_3 was smaller than 0.1 at 473 K before the reduction but increased to about 0.6 after reducing the catalyst with propylene at 773 K for 20 min; this is more evident for $x = 0.25$. The reduction effect was also obtained when a catalyst was reduced with hydrogen instead of propylene as shown in Fig. 4b with an open triangle where x was 0.1. That reduction was done at 823 K for 60 min. Kobylinski *et al.* found that metathesis selectivity is greatly enhanced by a prereduction with olefins (*7*). In our case, it is difficult to compare the effect of propylene and hydrogen as the surface concentration of oxygen vacancies was not known.

As a common trend, y increased with temperature for nonreduced catalysts and it decreased for reduced ones. The change in y after reduction was largest over $Na_{0.25}WO_3$ and that was from 0.002 to 1.00 at 473 K.

Adsorption of propylene was also investigated (Fig. 5 shows that on WO_3). The oxide was degassed at 473 K for 30 min under a vacuum of 10^{-7} Torr prior to an introduction of propylene at 1 atm. Adsorption of 1.5 mg corresponds to a one-to-one coverage of a propylene molecule over a tungsten ion. As is seen, only a little chemisorption was observed. Over $Na_{0.4}WO_3$ that was much smaller by more than one tenth and was hardly observed.

Through the experiments, it was found that Na_xWO_3 became harder to reduce as x increased. For instance, $Na_{0.4}WO_3$ could not be reduced appreciably with propylene even at 673 K for 60 min.

DISCUSSION

In a previous work (*1*), it was found that dimerization of propylene was dominant over WO_3 and metathesis was over ReO_3. WO_3 is an insulator and ReO_3 is electrically metallic. In this work it was intended to see whether the selectivity of the reaction changes discontinuously at $x = 0.25$ at which a metal–insulator transition occurs.

It was also found (*2*) that metathesis was enhanced when ReO_3 was slightly reduced and an oxygen vacancy was important for the reaction. Many authors already found that prereduction is very important to enhance the activity of metathesis over supported catalyst also (*8–15*). As the smaller particles of oxides on supports will have different physical properties compared to larger single crystals, it is not clear how the present result correlates with those. In case of unsupported oxides, a difficult problem is that an oxygen vacancy behaves as a donor and the conductivity is controlled both by Na ions and oxygen vacancies. Thus a boundary of the metal–insulator transition will shift to a smaller x than 0.25 when a catalyst is reduced.

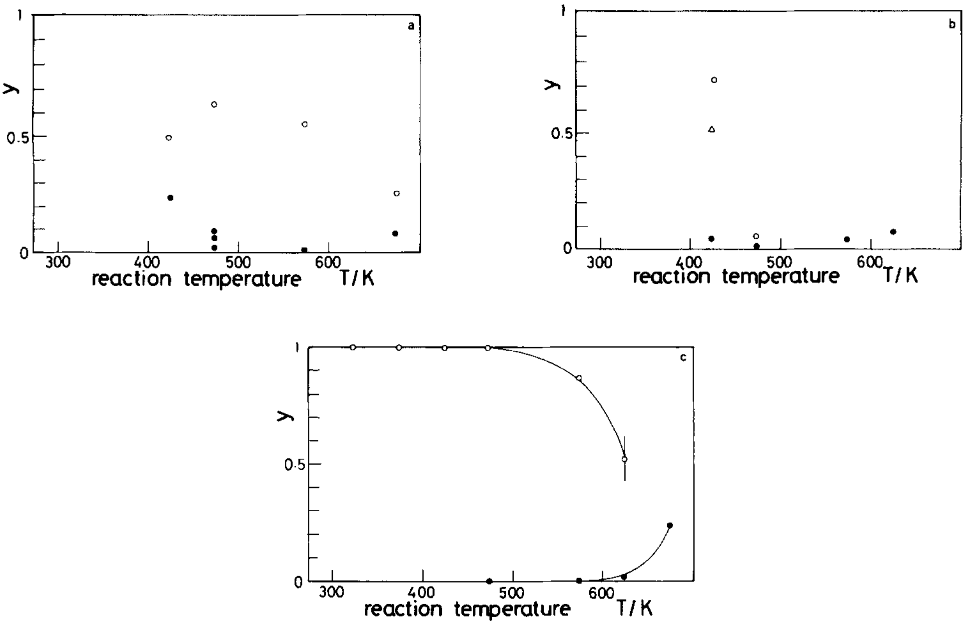

FIG. 4. a. Selectivity parameter y was plotted against reaction temperature. y is defined by Eq. (1) in the text. Solid symbols stand for as-prepared catalysts and open symbols for reduced ones in the increasing temperature. The catalyst was WO_3. Reduction was done with propylene at 773 K for 20 min. b. $Na_{0.1}WO_3$. Reduction was done with propylene at 573 K for 80 min (open circles). Open triangle stands for $Na_{0.1}WO_3$ reduced with hydrogen at 823 K for 60 min. c. $Na_{0.25}WO_3$. Reduction was done with propylene at 673 K for 80 min.

A mechanism of the transition is not clearly understood. However, a percolation view (*16, 17*) might be a suitable one whatever a mechanism of a localization of a conduction electron may be. In this view, Na ions are considered to distribute randomly and donated electrons localize on certain number of ions. When the concentration of donated electrons exceeds a critical value, 0.25 in this case, macroscopic conductive passes span a sample from one end to the other and it turns out to be metallic. Electrons are supplied nonthermally from Na ions and thermally from oxygen vacancies. The oxide is macroscopically homogeneous (*18*). A property of the localized electrons is not clear but we might consider that they do not localize on one tungsten ion each (*16*).

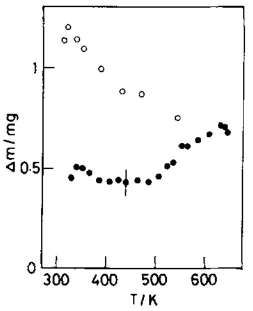

FIG. 5. Adsorption of propylene of 1 atm on WO_3. Solid and open symbols stand for adsorption in the increasing and decreasing temperature, respectively. The rate was 10 K/min. Adsorption of 1.5 mg corresponds to a monolayer coverage, that is, one propylene molecule over each tungsten ion.

Turning to the chemical reactions over unsupported catalysts, their characteristic features are small turnover numbers, oxygen vacancy dependences, and stereoselectivity of 2-butenes (*1, 2*). For instance, a turnover number over ReO_3 was less than 0.002 molecule/Re ion min at 473 K (*2*). That number might be underestimated because all Re ions were assumed to be active. If an amount of chemisorbed propylene was considered as an amount of active centers, it would have about one third of Re density. Thus though the turnover number might have been underestimated, it is still too small compared to those of supported catalysts (*13*). As for the stereoselectivity, *cis*-2-butene was produced more than *trans*-2-butene over ReO_3 (*2*).

The experimental results now will be discussed. The results in Fig. 4 show that reduction of oxides was very effective to enhance metathesis and to suppress dimerization. That was most drastic for $Na_{0.25}WO_3$ where metathesis replaced dimerization completely. That result suggests that metathesis and dimerization occurred at the same active points and both reactions were competing reactions. Otherwise both products will be expected to coexist. It must be noted that $Na_{0.25}WO_3$ became highly conductive after the reduction as shown in Fig. 2. It might not be so clear from Fig. 2 that the catalyst became metallic because the resistivity became smaller as temperature was raised as if that was a semiconductor. However, similar behavior was also observed for metallic $Na_{0.4}WO_3$. Moreover it is known that a sintered metallic material sometimes behaves as a semiconductor (*19*). Therefore $Na_{0.25}WO_3$ would have been metallic after the reduction considering the largeness of the change in the resistivity.

On oxides other than $Na_{0.25}WO_3$, the change from dimerization to metathesis was incomplete and both reactions coexisted. For these oxides, we did not obtain any conclusive data showing the occurrence of the metal–insulator transition. If the complete substitution of the chemical reaction over $Na_{0.25}WO_3$ is really due to the metal–insulator transition, that coexistence of metathesis and dimerization suggests that the distribution of oxygen vacancies is not homogeneous and metallic and nonmetallic regions coexist over the surfaces. This may be related to the experimental result which indicates that the oxides are harder to reduce as Na content is increased. Thus lattice oxygens which are located apart from Na ions may be removed through reduction first and the aggregation of them will be possible when Na content is low.

The selectivity of chemical reactions is mainly determined by a static property of electrons, that is, how HOMO's and LUMO's distribute energetically and spatially. However, our results show that a dynamical property of electrons may also be important to determine the selectivity. The importance of the relaxation effect was already pointed out by Shirley (*20*).

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