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SELECTIVE DEHYDROGENATION OF ETHANE BY NITROUS OXIDE OVER VARIOUS METAL OXIDE CATALYSTS

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Catalytic oxidation of ethane with N_2O in the presence of water has been investigated over various metal oxides. Zinc oxide showed a high catalytic activity for the oxidative dehydrogenation of ethane (52.0% conversion and 80.0% selectivity at 823K), while a 14.2% combined selectivity for acetaldehyde and ethanol formation was attained at a 8.9% conversion of ethane over a 2.1 wt% MoO_3/SiO_2 catalyst at 773K.

The selective oxidation of alkanes into alkenes is an important reaction both in fundamental and industrial catalyses. Oxygen or air has so far been used as the oxidant because it is cheap and readily available; however, selectivivies are often poor and reaction temperatures are high.[1] Although selective oxidative-dehydrogenation of ethane has been reported on V-Mo-Nb oxides by Thorsteinson et al.,[2] further confirmation or application of the reaction by other workers has never been reported. On the other hand, nitrous oxide is one oxidant that has been rarely used in the catalytic oxidation reactions. This lack of interest in N_2O as an oxidant may be a result of the supposed similarity in reactivities between N_2O and O_2, which is indeed the case over some catalysts at elevated temperatures.[3] However, it has very recently been reported that the two oxidants have extremely different activities[4,5] and also the oxide radical ion, O^-, which can be generated primarily in the decomposition of N_2O, shows higher reactivity than O_2^-, O_3^-, and O^{2-} ions.[6] We have therefore studied the oxidation of ethane over various metal oxides by N_2O, which will be of significant interest in the chemistry of active oxygen species. The same reaction has already been investigated by Lunsford and coworkers on MoO_3/SiO_2 catalysts,[5,7] but the yield of ethene was not so good.

Catalysts were prepared by conventional methods[8] and sieved to 42-80 mesh for use in the catalytic run. A mixture of C_2H_6, N_2O, and H_2O was passed through a fixed catalyst bed in a tubular flow reactor at an atmospheric pressure. Helium was used as the diluent. The reactants and products were analyzed by gas chromatography.

The typical results obtained at the reaction temperature of 823K are summarized in Table 1. The catalytic run was carried out under the following conditions; catalyst weight 1.0 g, total flow rate of gases 60 $cm^3 \cdot min^{-1}$, partial pressures of ethane 10.1 kPa, of N_2O 20.2 kPa, of H_2O 20.2 kPa, and of He 50.8 kPa, respectively. When the gases having the same composition was passed through the reactor without any catalyst, the extent of conversion of ethane was 5.6% and the major product was ethene. On the other hand, in non-oxidative dehydrogenation of ethane where an mixture of C_2H_6, H_2O,

Table 1. Catalytic Oxidation of Ethane by Nitrous Oxide over Various Metal Oxides at 823K.

Catalyst	Conversion (%)	Selectivity (%)						
		CH_4	C_2H_4	CH_3CHO	C_2H_5OH	C_4 + C_4' a)	CO	CO_2
CaO	7.3	3.2	85.8	0	0	6.4	2.7	1.9
TiO_2	6.3	0.9	61.8	tr.	0	1.3	33.0	3.0
V_2O_5	6.7	0.3	49.0	0.2	0	0.1	32.6	17.8
MnO_2	23.4	0.3	8.1	0.1	0	0	0	91.5
Fe_2O_3	36.3	0.3	38.1	0	0	0	0.1	61.5
Co_3O_4	34.7	0.5	21.9	0.1	0	tr.	0	77.5
NiO	100.0	10.7	0	0	0	tr.	24.2	58.3
CuO	26.4	0.7	1.4	0.1	0	0.5	0	97.3
ZnO	52.0	9.9	80.0	0.5	0	5.1	3.1	1.4
Bi_2O_3	16.3	2.4	88.0	0.2	0	5.4	0.8	3.1
SnO_2	38.9	1.4	29.7	0	0	0.7	1.2	67.0
V_2O_5/SiO_2 b)	16.6	1.4	57.3	1.3	tr.	0.3	22.3	17.3
MoO_3/SiO_2 c)	25.6	3.4	75.0	6.4	0.1	2.2	8.6	4.3
WO_3/SiO_2 d)	16.1	3.0	80.6	1.5	tr.	4.2	2.1	8.6

a) C_4 + C_4' represents the combined selectivity for butanes and butenes formation, b) 4.2 wt%, c) 2.1 wt%, d) 6.0 wt%.

and He, not containing N_2O, was made to flow over the various catalysts such as ZnO, Co_3O_4, and V_2O_5/SiO_2, at 823K, the levels of conversion of ethane and selectivity for ethene formation were 4.0-5.3% and 92-97%, respectively, irrespective of the kind of catalyst used. Both results indicate that all metal oxides listed in Table 1 show more or less catalytic activities for the oxidation of ethane by nitrous oxide. Among the metal oxides employed, NiO showed an unusual catalytic activity; the conversion of ethane was 85.9% at 773K and 100.0% at 823K. This relatively high conversions were confirmed to be due to a parallelly occurring steam-reforming reaction since 40.8% conversion of ethane and 80.5% selectivity for CO and CO_2 formation were attained at 823K in the absence of N_2O, and a large amount of hydrogen production accompanied by water consumption were also detected. This is reasonable by considering that NiO is used as an active component in the industrial steam-reforming processes.9)

On the basis of the catalytic results summarized in Table 1, one can divide the catalysts into three groups as followes,

(A) metal oxides which showed relatively high catalytic activities with high selectivity for ethene formation; Fe_2O_3, ZnO, Bi_2O_3, MoO_3/SiO_2, V_2O_5/SiO_2, and WO_3/SiO_2,

(B) metal oxides which showed high catalytic activities but low yields of ethene; MnO_2, Co_3O_4, NiO, CuO, and SnO_2,

(C) low active metal oxide catalysts; CaO, TiO_2, V_2O_5, MoO_3, and WO_3.

It is evident that MoO_3, V_2O_5, and WO_3 exhibited high activities only when they were supported on silica gel; the degree of the conversion of ethane over unsupported V_2O_5 catalyst is shown in the table as an example. The result of X-ray diffraction analysis revealed that CuO catalyst changed to Cu_2O during the course of the catalytic run, indicating that the working state of CuO was Cu_2O. The above classification is roughly correlated with the order of the catalytic activities of metal oxides for the decomposition of N_2O reported by several workers,$^{10)}$ which suggests the close similarity in the reaction mechanisms and/or rate determining steps to exist between the catalytic oxidation of ethane by N_2O and the catalytic decomposition of N_2O, though the reaction scheme of ethane with N_2O remains unclarified.

Yang and Lunsford$^{5)}$ have recently reported the oxidation of ethane by N_2O over MoO_3/SiO_2 catalysts and obtained 11.7% conversion of ethane and 64% selectivity for ethene at 748K. The results shown in Table 1 are better than these, though the reaction temperatures were different. It was confirmed in a separate experiment that the difference between the present and Yang's results was due to the presence of water vapor in the reaction system; the rate of formation of carbon monoxide and carbon dioxide without the water addition was approximately twice as great as that with the water addition, while the rate of formation of ethene did not change so much regardless of the presence or absence of water.

It would be noteworthy that the combined selectivity for acetaldehyde and ethanol formation was 14.2% at the 8.9% conversion of ethane over MoO_3/SiO_2 although the reaction conditions were the same as that in the Table except the lowered temperature of 773K. Therefore the direct oxidation of ethane to oxygen-containg organic compounds is clearly possible by using N_2O as an oxident but not so selective as that of methane to methanol and formaldehyde.$^{11)}$ This would be attributable to the difference of the reactivities and/or stabilities of the surface intermediates produced after the first dehydrogenation of ethane and methane; the possible intermediate from ethane, $\dot{C}_2H_5$, would readily undergo a second dehydrogenation to yield ethene, while the methyl radical from methane, $\dot{C}H_3$, might be difficult to release one more hydrogen so that it would be coupled with surface hydroxyl groups to give methanol.

Finally, the reaction of ethane with O_2 was examined for the comparison of that with N_2O. A mixture of C_2H_6 (10.1 kPa), O_2 (10.1 kPa), H_2O (20.2 kPa), and He (60.9 kPa) was introduced into the reactor at the same conditions as those in Table 1. With 5 wt% V_2O_5/SiO_2 or ZnO as the catalyst, the conversion of ethane and selectivity for ethene formation were 65.1 and 57.5% or 68.5 and 63.3%, respectively. However, even without any catalyst the conversion and selectivity were 64.4 and 66.9%, respectively. These were very close to the above values, indicating that in the reaction of ethane with O_2 at a high temperature noncatalytic homogeneous gas-phase reactions were more important than catalytic oxidation processes. In addition, it would be noteworthy that only trace amounts of acetaldehyde and ethanol were observed in all experiments using O_2 as an oxidant. Although the mechanism for the oxidation of ethane involving O_2 is unknown and no evidence was obtained for the reaction mechanism of N_2O, we wish to suggest that the relatively high selectivity for ethene, ethanol and acetaldehyde formation result from reactive O^- intermediates which could be easily generated through the decomposition of N_2O in the presence of available electrons.$^{12)}$

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