

IMPORTANCE OF SURFACE OXYGEN UNDETECTABLE WITH ESR ON Co-MgO
FOR OXIDATIVE DEHYDROGENATION OF ETHANE

Ken-ichi AIKA,* Masaki TAJIMA, and Takaharu ONISHI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

Adsorbed oxygen, which is produced from N_2O on Co-MgO and does not show any ESR signals, was found to be active for the oxidative dehydrogenation of ethane as well as O^- which is observable with ESR. Since the adsorbed oxygen can only be regenerated in the catalysis condition, it should be a reactive oxygen species involved in the catalytic cycle of this reaction.

O^- has been discussed to be a plausible active species for the partial oxidation reactions of alkanes by N_2O on various oxides,¹⁻³⁾ mostly because surface O^- has been reported to react with alkanes by abstracting hydrogen on a MgO surface.⁴⁾ However, there has not been any direct evidences of O^- which is involved in the catalytic reaction carried out at 500 to 600 °C.¹⁻³⁾

It has been reported that O^- is formed from N_2O on thermally activated Co-MgO⁵⁾ which is known to be an active catalyst for N_2O decomposition.⁶⁾ Thus we can have various kinds of active oxygen species (O^- , O_2^- , lattice oxygen, adsorbed oxygen etc.) on the same catalyst (Co-MgO) depending on the surface condition. We examined the reactivity of various surface oxygens against ethane, and tried to relate the surface reaction with the catalytic reaction. ESR signal of O^- formed on 900 °C-evacuated 0.2 atom% Co-MgO disappeared when ethane was introduced at 25 °C. Ethylene (mostly up to 300 °C) and methane (up to 500 °C) were obtained as products by TPD run after the surface reaction. Since test compounds CH_3CHO and C_2H_5OH were decomposed to form CH_4 and C_2H_4 respectively as a main product during TPD run on Co-MgO, the surface intermediates of the reaction between ethane and O^- on Co-MgO were considered to be the mixture of both CH_3COO^- and $C_2H_5O^-$, which is

different from the case on MgO.⁴⁾ O_3^- was detected with ESR when O_2 was introduced on $O^-/Co-MgO$. O_2^- was also detected when O_2 was introduced on 900 °C-evacuated Co-MgO. O^- was not observed on 500 °C-evacuated Co-MgO even though N_2O was decomposed to leave adsorbed oxygen at 25 °C. To those various kinds of oxygen species, ethane was introduced and the resultant surface reaction products were analyzed by TPD as is shown in Table 1. O^- concentration was measured by using P/Si as a standard material as has been reported.⁴⁾

Table 1. Surface Reactivity^{a)} of Various Oxygens against Ethane on Co-MgO^{b)}

Sample code	Evacuation condition °C/h	Oxidant source	Proposed form/ g-value	O^- conc. (nmol/g)	TPD products (nmol/g) ^{c)}		
					C_2H_4	$CH_4/2$	Total ^{d)}
1	900/3.5	N_2O	$O^-/2.045, 2.002^h)$	58	33	165	198
2	900/3	N_2O	$O^-/2.045, 2.002$	35	35	58	93
3 ^{e)}	500/0.5	N_2O	--	neg ^{k)}	24	34	58
4 ^{f)}	500/0.5	N_2O	--	neg	8	7	15
5	500/3.5	N_2O	--	neg	8	8	16
6	900/3.5	no	O^{2-} (lattice)	neg	neg ^{k)}	neg ^{k)}	neg ^{k)}
7	900/3.5	O_2	$O_2^-/2.07, (2.09)$ $2.009, 2.002^i)$	neg	neg	neg	neg
8	900/3.5	N_2O/O_2	$O_3^-/2.018, 2.010,$ $2.003^j)$	neg	20	neg	20
9 ^{g)}	25/0.5	N_2O	--	neg	20	2	22

a) Co-MgO was evacuated at 500 or 900 °C, then cooled to 25 °C where oxidant was adsorbed and evacuated. After ESR measurement, about 1.9 μ mol of ethane was introduced at 25 °C and TPD was carried out up to 500 °C. b) 2 g of 0.2 atom % Co-MgO was used. c) Amounts after 500 °C heating; Most of ethylene was obtained up to 300 °C. d) $(C_2H_4)+(CH_4)/2$. e) Run after TPD of 2. f) Run after TPD of 3. g) Run after catalytic reaction (N_2O/C_2H_6) at 200 °C. h) Reported g-values are 2.042, 2.0013 for MgO⁷⁾ and 2.047, 2.0014 for 1% Co-MgO.⁵⁾ i) Reported g-values are 2.077, 2.007, 2.001 for MgO^{8, 9)} and 2.075, (2.098), 2.008, 2.0017 for 1% Co-MgO.⁵⁾ The spectra had no hyperfine with Co^{2+} . j) Reported g-values are 2.0172, 2.0100, 2.0014 for MgO¹⁰⁾ and 2.017, 2.012, 2.0025 for 1% Co-MgO.⁵⁾ k) Value below about 1 nmol/g.

The following results are summarized.

- 1) Reactivity sequence of anion radicals on Co-MgO is the same as those on MgO^{11, 12}); i. e., $O^-(\text{sample 1}) > O_3^-(\text{sample 8}) > O_2^-(\text{sample 7})$. Adsorbed O_2 containing O_2^- does not react with ethane.
- 2) Lattice oxygen does not react with ethane (sample 6).
- 3) Although O^- has been reported to react with ethane stoichiometrically on MgO (one to one)⁴), the amounts of products in this study are much higher than the O^- concentrations (sample 1, 2). The existence of active oxygen other than O^- is suggested.
- 4) Adsorbed oxygen from N_2O which gives no ESR signal is also reactive to ethane and gives similar TPD products although the amount of product is not much (sample 3, 4, 5, 9).

It is necessary to evacuate the sample at more than 750 °C in order to obtain O^- from N_2O on Co-MgO. Thus formed O^- can react with ethane only once, but it can not be regenerated under the catalysis condition with the temperature below 700 °C. Under the catalysis condition, the adsorbed active oxygen which is not observed by ESR (sample 3, 4, 5, 9) must be more important. Such oxygen has been discussed to be located on a MgO surface.⁶) Because of the similarity of the reactivity to those of O^- , the form of adsorbed oxygen is considered to resemble O^- in its electronic structure; presumably O^- with the charge partially transferred. However, further studies should be necessary to clarify the nature of the undetected oxygen.

Table 2. Oxidative Dehydrogenation Reaction of Ethane by N_2O ^{a)}

Catalyst (2g)	Pretreatment	C_2H_4 %yield	C_2H_4 %select.	N_2O %conv.	C_2H_6 %conv.
0.2% Co-MgO	500 °C evac.	15	94	32	16
0.2% Co-MgO	900 °C evac.	7.0	63	23	11
0.2% Co-MgO	900 °C evac./ O_2 ^{b)}	(2)	(14)	(30)	(14)
MgO	900 °C evac.	3.6	92	14	3.7
0.5% Co-SiO ₂	900 °C evac.	0	0	14	11

a) C_2H_6 and N_2O (or O_2) with both 0.32 mmol(50 Torr) were reacted for 1 h at 200 °C. b) O_2 was used instead of N_2O .

Finally a reaction between N_2O and C_2H_6 was carried out catalytically at 200 °C. As is shown in Table 2, 0.2% Co-MgO was proved to be an effective catalyst for oxidative dehydrogenation of ethane at as low as 200 °C when N_2O was used as an oxidant. By using O_2 , the ethylene selectivity was poor. Judging from the less selectivity of 0.2% Co-SiO₂, MgO in Co-MgO plays an important role giving an active oxygen species for this reaction. After the catalytic reaction at 200 °C, the used catalyst was characterized by ESR and TPD techniques (sample 9) in a similar method to that for sample 1 to 8 (in Table 1). On the used catalyst, O^- was not observed by ESR. However, the adsorbed oxygen reacted with ethane forming similar TPD products to those for the 500 °C-evacuated samples. Thus, the adsorbed oxygen from N_2O which shows no ESR signal is considered to be important and can be involved in the catalytic cycle of the oxidative dehydrogenation on Co-MgO.

This investigation was partly supported by a Grant-in-Aid for Scientific Research (No. 57212010) from the Ministry of Education, Science, and Culture. We also acknowledge the contribution of Mr. M. Isobe.

References

- 1) R. -S. Liu, M. Iwamoto, and J. H. Lunsford, *J. Chem. Soc., Chem. Commun.*, 1982, 78.
- 2) M. Iwamoto, T. Taga, and S. Kagawa, *Chem. Lett.*, 1982, 1469.
- 3) M. Iwamoto, J. Hirata, K. Matsukami, and S. Kagawa, *J. Phys. Chem.*, 87, 903 (1983).
- 4) K. Aika and J. H. Lunsford, *J. Phys. Chem.*, 81, 1393 (1977).
- 5) V. Indovina, D. Cordischi, M. Occhiuzzi, and A. Arieti, *J. Chem. Soc., Faraday Trans. 1*, 75, 2177 (1979).
- 6) A. Cimino and F. Pepe, *J. Catal.*, 25, 362 (1972).
- 7) N. B. Wong and J. H. Lunsford, *J. Chem. Phys.*, 55, 3007 (1971).
- 8) J. H. Lunsford and J. P. Jayne, *J. Chem. Phys.*, 44, 1487 (1966).
- 9) A. J. Tench and P. J. Holroyd, *J. Chem. Soc., Chem. Commun.*, 1968, 471.
- 10) N. B. Wong and J. H. Lunsford, *J. Chem. Phys.*, 56, 2664 (1972).
- 11) Y. Takita and J. H. Lunsford, *J. Phys. Chem.*, 83, 683 (1979).
- 12) M. Iwamoto and J. H. Lunsford, *J. Phys. Chem.*, 84, 3079 (1980).

(Received August 20, 1983)