[Regular Paper]

Catalytic Activities of Single Component Metal Oxides for Selective Reduction of NO with Ethene

Noriyasu OKAZAKI*, Takeshi SASAKI, Yoshiki KATOH, and Akio TADA

Dept. of Applied and Environmental Chemistry, Kitami Institute of Technology, Kitami 090-8507, JAPAN

(Received December 5, 2001)

The catalytic activities of thirteen types of single component metal oxides were measured for the selective catalytic reduction (SCR) of NO with ethene in excess oxygen and related reactions to elucidate the characteristic features of catalyst activity. The related reactions were the oxidation of NO₂ with O₂, the oxidation of C₂H₄ with O₂, the reduction of NO₂ with C₂H₄ in the absence of O₂, and the reduction of NO with C₂H₄ in the absence of O₂. Alumina exhibited the highest activity for SCR, followed by ZrO₂, SnO₂, MgO, CaO, Y₂O₃, and TiO₂; WO₃, Co₃O₄, CuO, Fe₂O₃, ZnO, and SiO₂ showed little activity. The active catalysts including alumina had the characteristic features of high activities for both the oxidation of NO to NO₂ and the reduction of NO₂ with C₂H₄ to form N₂, as well as low activity for the oxidation of C₂H₄ with O₂. Although Co₃O₄, CuO, and Fe₂O₃ showed high activities for the oxidation of NO to NO₂, they were also highly active for the oxidation of C₂H₄ with O₂. Therefore, C₂H₄ was consumed without reduction of NO over these catalysts. The characteristic features for the active catalysts also support the reaction scheme that the SCR proceeds by the successive reactions of the oxidation of NO to NO₂ and the reduction of NO₂ with C₂H₄ to form N₂.

Keywords

Nitrogen monoxide, Selective catalytic reduction, Hydrocarbon, Ethene, Metal oxide catalyst, Alumina catalyst

1. Introduction

Cu-ZSM-5 was proposed as an active catalyst for selective catalytic reduction of NO with hydrocarbons many years ago^{1)~3),4)}. Later, H-ZSM-5 and alumina were also shown to display considerable activities for the reaction⁵⁾. Both H-ZSM-5 and alumina have on the surface acidic sites, which may participate in the reaction⁵⁾.

The following reaction scheme was proposed in which three reactions are involved in the reduction of NO with propane over alumina⁵⁾.

Selective reduction of NO with hydrocarbons requires that reactions (1) and (2) occur in the same temperature range, and reaction (3) should be minimized. Presumably a catalyst for the reduction of NO with hydrocarbons will be active for reactions (1) and (2), and inactive for reaction (3).

Review of the catalytic behaviors of metal oxide type

catalysts classified the single component metal oxides into two types^{6),7)}. One type includes the metal oxides with high activity for oxygen activation such as the oxides of Co, Fe, and Cu. However, these catalysts exhibit essentially no catalytic activity for the selective reduction of NO with hydrocarbons. The other type includes the metal oxides with acid-base properties such as the oxides of Al, Ti, Zr, Zn, Mg, and rare earth elements. These catalysts exhibit relatively high activity for the selective reduction of NO with hydrocarbons. Alumina has the highest activity among the metal oxides.

The catalytic activity of alumina is enhanced by modification with transition metals or transition metal oxides such as Ag^{8)~10)}, Co^{11)~13)} and Pt¹⁴⁾. Highly active catalysts contain alumina as one of the components, usually as a support for the transition metals or metal oxides. However, the characteristic features of alumina, in contrast to the other single component metal oxides, have not been systematically clarified.

The present study investigated the catalytic activities of different types of metal oxide for the reduction of NO with hydrocarbon and the three key reactions to elucidate the required catalytic features. Ethene was selected as the hydrocarbon because ethene is more

* To whom correspondence should be addressed.

* E-mail: zaki@catal.chem.kitami-it.ac.jp

abundant than propane and propene in the exhaust gas from a gasoline engine.

2. Experimental Method

2.1. Preparation of Catalysts

Alumina was prepared from aluminum tri-isopropoxide by hydrolysis with deionized water. Aluminum tri-isopropoxide was purchased from Koujundo Chem. Lab. Co., Ltd. and purified by repeated distillation three times. The purified aluminum tri-isopropoxide was poured dropwise into deionized water kept at 273 K with vigorous stirring. Aluminum hydroxide was precipitated. The precipitate was filtered and washed thoroughly with deionized water. The resulting material was dried at 383 K for 24 h, and then calcined at 873 K for 24 h in air to form alumina.

Co₃O₄ was prepared from Co(NO₃)₂ by precipitation with ammonia solution. Co(NO₃)₂·6H₂O was purchased from Kishida Chem. Co. Aqueous ammonia was added dropwise to an aqueous solution of cobalt nitrate until the pH of the solution reached 7. The precipitate was filtered and washed thoroughly with deionized water. The resulting material was dried at 383 K for 24 h, pressed into pellets followed by crushing and sieving to 30-42 mesh, and then calcined at 773 K for 24 h in air to form Co₃O₄.

ZrO₂ was prepared from ZrCl₂O by precipitation with ammonia solution. ZrCl₂O·8H₂O was purchased from Kishida Chem. Co. The following procedures were the same as for Co₃O₄.

CuO was prepared from Cu(NO₃)₂ by precipitation with urea solution. Cu(NO₃)₂·3H₂O was purchased from Kishida Chem. Co. Three molar equivalents of urea were added to Cu(NO₃)₂ solution, and the mixture heated above 368 K for 12 h with vigorous stirring. The precipitate was filtered and washed thoroughly with deionized water. The resulting material was dried at 383 K for 24 h, pressed into pellets followed by crushing and sieving to 30-42 mesh, and then calcined at 773 K for 24 h in air to form CuO.

Fe₂O₃ was prepared from Fe(NO₃)₃ by precipitation with urea solution. Fe(NO₃)₃·9H₂O was purchased from Kishida Chem. Co. The following procedures were the same as for CuO.

CaO was prepared from Ca(NO₃)₂ by precipitation with urea solution. Ca(NO₃)₂·4H₂O was purchased from Kishida Chem. Co. The following procedures were the same as for CuO.

The following oxides were purchased: SnO₂ and WO₃ from Koujundo Chem. Lab. Co., Ltd., MgO from Kanto Chem. Co., Inc., SiO₂ from Nishio Kougyo Co., Ltd., TiO₂ P-25 from Aerosil, Y₂O₃ from Furuuchi Chem. Co., and ZnO from Wako Pure Chem. Ind., Ltd. These oxides were pressed into pellets followed by crushing and sieving to 30-42 mesh.

Table 1 Surface Area and Crystalline Structures of Metal Oxides

Catalyst	Surface area [m ² ·g ⁻¹]	Crystalline structure
Al ₂ O ₃	145	γ-Al ₂ O ₃ (cubic)
CaO	35	CaO (cubic)
Co ₃ O ₄	13	Co ₃ O ₄ (cubic)
CuO	25	CuO (monoclinic)
Fe ₂ O ₃	7	Fe ₂ O ₃ (rhombohedral)
MgO	76	MgO (cubic)
SiO ₂	166	Amorphous
SnO ₂	6	SnO ₂ (tetragonal)
TiO ₂	11	TiO ₂ (tetragonal)
WO ₃	10	WO ₃ (monoclinic, triclinic)
Y ₂ O ₃	7	Y ₂ O ₃ (cubic)
ZnO	1	ZnO (monoclinic)
ZrO ₂	16	ZrO ₂ (monoclinic, orthorhombic)

All catalysts were calcined at 1073 K before use in the experiments, for surface area measurement, and for XRD measurement.

Surface areas of the metal oxides were measured by the BET method. X-Ray diffraction patterns of the metal oxides were measured using a RINT-1200 diffractometer (Rigaku International Co.), using CuKα as the X-ray source.

2.2. Reaction Procedures

All reactions were carried out in a fixed bed flow reactor at a *W/F* of 0.18 g·s·cm⁻³ (catalyst, 0.40 g; total flow rate, 130 cm³·min⁻¹) at temperatures ranging from 573 to 1073 K. All catalysts were heated at 1073 K for 4 h in air before catalytic runs, then placed in the quartz tube reactor (inner diameter, 6 mm) with quartz wool plugs and heated in a He stream (30 cm³·min⁻¹) at 573 K for 0.5 h just before the catalytic runs. The reactant gas (NO or NO₂, 0 or 1000 ppm; O₂, 0 or 2.0%; C₂H₄, 0 or 500 ppm; He, balance) was passed through the catalyst bed. The outflow gases during the reactions except for NO+O₂ were analyzed by gas chromatography using 5A molecular sieves (3 m; separation for N₂, O₂, CO and NO) and Porapak Q (3 m; separation for CO₂, C₂H₄ and N₂O). The outflow gas during NO+O₂ was analyzed by FT-IR.

3. Results

3.1. Surface Area and Structure of Metal Oxides

The surface areas and crystalline structures measured by XRD are listed in **Table 1**. All prepared catalysts consisted of metal oxides in various crystalline structures. SiO₂ did not show definite X-ray patterns, but was believed to be the amorphous oxide.

3.2. Reduction of NO with C₂H₄ in Excess O₂

The catalytic activities of thirteen types of single component metal oxide for the reduction of NO with C₂H₄ in excess O₂ were measured in the temperature

Reaction conditions: NO = 1000 ppm, C₂H₄ = 1000 ppm, O₂ = 2%, catalyst weight = 0.4 g, W/F = 0.18 g·s·cm⁻³.

Fig. 1 Temperature Dependence of the Catalytic Activities of Various Metal Oxides for NO+C₂H₄+O₂

Reaction conditions: NO = 1000 ppm, O₂ = 2%, catalyst weight = 0.4 g, W/F = 0.18 g·s·cm⁻³.

Fig. 3 Temperature Dependence of the Catalytic Activities of Various Catalysts for NO+O₂

Reaction conditions: NO = 1000 ppm, C₂H₄ = 1000 ppm, O₂ = 2%, catalyst weight = 0.4 g, W/F = 0.18 g·s·cm⁻³.

Fig. 2 Temperature Dependence of the Catalytic Activities of Various Catalysts for NO+C₂H₄+O₂

range 473–1073 K. The conversions of NO to N₂ are plotted against the reaction temperature in Fig. 1. For all catalysts, the conversion increased with higher reaction temperature to reach a maximum, and then decreased on further increase in the temperature. The maximum conversion and the associated reaction temperature varied with the type of catalyst. The order of catalytic activity according to the maximum conversion was as follows;

Al₂O₃ > ZrO₂ > SnO₂ > MgO, CaO, Y₂O₃ > TiO₂ > WO₃, Co₃O₄, CuO, Fe₂O₃, ZnO, SiO₂

Alumina exhibited the highest conversion to N₂, followed by ZrO₂, SnO₂, MgO, CaO, and Y₂O₃. WO₃, Co₃O₄, CuO, Fe₂O₃, ZnO, and SiO₂ showed little activity for N₂ formation.

The conversion of C₂H₄ to CO and CO₂ over the thirteen catalysts as a function of the reaction temperature showed different profiles from those for the conversion

of NO to N₂ as shown in Fig. 2. With Co₃O₄, CO_x (CO and CO₂) began to form at a reaction temperature of 423 K, and all C₂H₄ was consumed at 573 K. Consumption of C₂H₄ to form CO and CO₂ occurred through both the reaction of C₂H₄ with O₂ and the reaction of C₂H₄ with NO or NO₂. The order of catalytic activity for the CO_x formation according to the temperature for 20% conversion to CO_x was as follows;

Co₃O₄ > CuO > Fe₂O₃ > SnO₂ > Al₂O₃ > ZrO₂ > Y₂O₃, MgO, CaO, ZnO, SiO₂, TiO₂, WO₃

With Co₃O₄, CuO, and Fe₂O₃, the formation of CO_x occurred at relatively low temperatures, and little formation of N₂ was observed, indicating that C₂H₄ was consumed by the reaction with O₂, and not by the reaction with NO or NO₂. With Al₂O₃, ZrO₂, and SnO₂ which exhibit high activity for the reduction of NO to N₂, the formation of CO_x occurred in the same temperature range as the reduction of NO to N₂. Considerable amounts of C₂H₄ were consumed for the reduction of NO or NO₂ to N₂. With the metal oxides such as WO₃, ZnO, and SiO₂ which showed little activity for the reduction of NO to N₂, the formation of CO_x occurred at high temperature. Consumption of C₂H₄ occurred by the reaction of C₂H₄ with O₂. The reactions of NO and NO₂ with C₂H₄ should not occur at temperatures lower than the temperature required for the reaction of C₂H₄ with O₂.

3.3. Oxidation of NO with O₂ to form NO₂

According to the reaction scheme proposed by Hamada *et al.*⁵⁾, NO is oxidized to form NO₂ which then reacts with C₂H₄ to form N₂. The activities of the single component metal oxides for the oxidation of NO were measured to find any correlation between the activity for the reduction of NO with C₂H₄ and the activity for the oxidation of NO. The results are shown in Fig. 3 in which the conversions of NO to NO₂ are plotted against the reaction temperatures.

Reaction conditions: $C_2H_4 = 1000$ ppm, $O_2 = 2\%$, catalyst weight = 0.4 g, $W/F = 0.18 \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$.

Fig. 4 Temperature Dependence of the Catalytic Activities of Various Catalysts for $C_2H_4+O_2$

The dotted line indicates the equilibrium conversion.

The order of the activity was as follows;

$Co_3O_4 \gg CuO, Fe_2O_3 \gg SnO_2 > ZrO_2 > Y_2O_3 > CaO > Al_2O_3, MgO > TiO_2 > WO_3 > SiO_2$

This order is approximately the same as that for the formation of CO_x in the reduction of NO with C_2H_4 in the presence of O_2 . However, the catalysts with high activity for the oxidation of NO, such as Co_3O_4 , CuO, and Fe_2O_3 , were not so active for the reduction of NO. The catalysts active for the reduction of NO were also active for the oxidation of NO to NO_2 in the same reaction temperature range. For example, Al_2O_3 exhibited considerable activity for the reduction of NO in the temperature range 723–923 K, in which the activity for the oxidation of NO was also appreciable.

3. 4. Oxidation of C_2H_4 with O_2

Efficient use of C_2H_4 for the reduction of NO requires suppression of the oxidation of C_2H_4 with O_2 . The activities of the single component metal oxides for the oxidation of C_2H_4 with O_2 were measured as a function of the reaction temperature as shown in Fig. 4. The order of catalytic activity for the oxidation of C_2H_4 according to the temperature for 20% conversion to CO_x was as follows;

$Co_3O_4 > CuO > Fe_2O_3 > SnO_2 > ZrO_2 > Al_2O_3 > Y_2O_3 > MgO > CaO > ZnO > SiO_2 > TiO_2 > WO_3$

This order is approximately the same as that of the activity for the oxidation of NO with O_2 to form NO_2 . The catalysts with high activity for the oxidation of C_2H_4 are not active for the reduction of NO with C_2H_4 in excess O_2 . For these catalysts, C_2H_4 was consumed for the reaction with O_2 , and not for the reduction of NO.

3. 5. Reduction of NO_2 with C_2H_4 in the Absence of O_2

If the reduction of NO proceeds by the successive reactions (1) and (2), active catalysts for the reduction

Reaction conditions: $NO_2 = 1000$ ppm, $C_2H_4 = 1000$ ppm, catalyst weight = 0.4 g, $W/F = 0.18 \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$.

Fig. 5 Temperature Dependence of the Catalytic Activities of Various Catalysts for $NO_2+C_2H_4$

Reaction conditions: $NO = 1000$ ppm, $C_2H_4 = 1000$ ppm, catalyst weight = 0.4 g, $W/F = 0.18 \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$.

Fig. 6 Temperature Dependence of the Catalytic Activities of Various Catalysts for $NO+C_2H_4$

of NO should promote the reaction of NO_2 with C_2H_4 in the same temperature range as that of the oxidation of NO to NO_2 . The activities of the single component metal oxides were measured, and the results are shown in Fig. 5 in which the conversions of NO_2 are plotted against the reaction temperature. The order of the activity was as follows;

$Al_2O_3 > SnO_2 > ZrO_2 > Y_2O_3 > CaO > ZnO \gg Co_3O_4, CuO, Fe_2O_3, SiO_2, WO_3, TiO_2, MgO$

Alumina exhibited the highest activity in the same temperature range for the reduction of NO and the reaction of NO_2 with C_2H_4 . The catalysts with high activity for the oxidation of NO and C_2H_4 with O_2 , such as Co_3O_4 , CuO, and Fe_2O_3 , were not active for the reaction of NO_2 with C_2H_4 .

3. 6. Reaction of NO with C_2H_4 in the Absence of O_2

The results are shown in Fig. 6. Co_3O_4 , CuO, and

Fe_2O_3 exhibited considerable activities in the temperature range 473–773 K, but the other catalysts did not catalyze the reaction in the temperature range in which the reduction of NO with C_2H_4 in excess O_2 occurs. However, reduction of the catalysts occurred during the reaction. Possibly the lattice oxygen atoms are utilized for the oxidation of NO over these catalysts. For alumina, the activity became appreciable at 773 K, and the conversion of NO to N_2 in the reaction of NO with C_2H_4 was far less than in the reaction of NO with C_2H_4 in the presence of O_2 and in the reaction of NO_2 with C_2H_4 .

4. Discussion

Among the thirteen types of single component metal oxides examined in the present study, alumina was the most active catalyst for the reduction of NO with C_2H_4 in excess O_2 , whereas Co_3O_4 , CuO , and Fe_2O_3 showed little activity, as reported previously by Hamada *et al.*⁶⁾

The characteristic features of alumina for the three key reactions are as follows;

- Alumina has considerable catalytic activity for the oxidation of NO with O_2 in the temperature range 723–923 K.
- Alumina has considerable catalytic activity for the reduction of NO_2 with C_2H_4 in the temperature range 723–923 K.
- Alumina promotes the oxidation of C_2H_4 with O_2 , but the temperature at which the oxidation of C_2H_4 to CO_x occurs is higher than the temperature at which the oxidation of NO to NO_2 occurs.

To examine whether characteristic feature (c) is observable for the other catalysts which exhibited relatively high activity, the relative activity for oxidation of C_2H_4 with O_2 to that for oxidation of NO with O_2 to NO_2 were plotted against the activity for the reduction of NO with C_2H_4 in excess O_2 . The difference between the temperature for 50% conversion for the oxidation of C_2H_4 and the temperature for the maximum conversion for the oxidation of NO was used as a measure of the relative activity for the oxidation reactions. The maximum conversion for the reduction of NO with C_2H_4 in excess O_2 was used as a measure of the activity for the reduction of NO with C_2H_4 in excess O_2 . The plots are shown in Fig. 7. If the temperature difference was positive, oxidation of NO occurred relatively quickly compared to the oxidation of C_2H_4 . In contrast, if the temperature difference was negative, oxidation of C_2H_4 occurred preferentially to the oxidation of NO. The catalysts with positive temperature differences had high activity for the reduction of NO with C_2H_4 in excess O_2 , and those with negative temperature differences had almost no activity except for SnO_2 . Although this kind of plot shows only the qualitative trend, it is suggested that the catalysts rather

T_1 : Temperature for 50% conversion of $\text{C}_2\text{H}_4 + \text{O}_2 \rightarrow \text{CO}_x$.

T_2 : Temperature for maximum conversion of $\text{NO} + \text{O}_2 \rightarrow \text{NO}_2$.

Fig. 7 Temperature Difference $T_1 - T_2$ vs. Maximum Conv. for $\text{NO} + \text{C}_2\text{H}_4 + \text{O}_2$

active for the reduction of NO with C_2H_4 in excess oxygen have catalytic properties that the oxidation of NO prefers to the oxidation of C_2H_4 . This is expected if the reduction of NO with C_2H_4 in excess O_2 proceeds by the reactions (1) and (2).

With Co_3O_4 , CuO , and Fe_2O_3 , the oxidation of C_2H_4 proceeded more rapidly than the oxidation of NO, so C_2H_4 was consumed mostly for the reaction with O_2 to form CO_x . Therefore, Co_3O_4 , CuO , and Fe_2O_3 show little activity for the reduction of NO with C_2H_4 in excess O_2 . With TiO_2 , WO_3 , ZnO , and SiO_2 , which also exhibit only low activities for the reduction of NO with C_2H_4 in excess O_2 , the oxidation of NO to form NO_2 hardly proceeds. These catalysts also have low activities for the reduction of NO with C_2H_4 in the absence of O_2 . In addition, they are almost inactive for the reaction of NO_2 with C_2H_4 .

Plotting of the conversions in the oxidation of C_2H_4 and the oxidation of NO_2 on the same figure for Al_2O_3 and Co_3O_4 , which are representatives of “active catalyst” and “inactive catalyst” for the reduction of NO with C_2H_4 in excess O_2 , indicates the necessary properties for an active catalyst. These plots are shown in Figs. 8 and 9 for Al_2O_3 and Co_3O_4 , respectively. For Al_2O_3 , the oxidation of NO with O_2 to NO_2 clearly occurs in a lower temperature range than the oxidation of C_2H_4 with O_2 to CO_x . On the other hand, for Co_3O_4 , the oxidation of C_2H_4 occurs in a lower temperature range than the oxidation of NO. As mentioned above, the main reason for the high activity of Al_2O_3 is the definite separation in the temperature range in which the oxidation of C_2H_4 and the oxidation of NO occur. The activity of a catalyst could be increased by modification of the alumina to enlarge the separation in the temperature range between the oxidation of NO to

Reaction conditions: NO = 1000 ppm, C₂H₄ = 1000 ppm, O₂ = 2%, catalyst weight = 0.4 g, W/F = 0.18 g·s·cm⁻³.

Fig. 8 Temperature Dependence of the Catalytic Activities of Al₂O₃

Reaction conditions: NO = 1000 ppm, C₂H₄ = 1000 ppm, O₂ = 2%, catalyst weight = 0.4 g, W/F = 0.18 g·s·cm⁻³.

Fig. 9 Temperature Dependence of the Catalytic Activities of Co₃O₄

NO₂ and the oxidation of C₂H₄ to CO_x. Such the modification should result in an increase in the activity for the oxidation of NO and a decrease in the activity for the oxidation of C₂H₄. More desirably, the modification may increase the reaction of NO₂ with C₂H₄.

The surface properties controlling the three key reactions, the oxidation of NO with O₂ to NO₂, the oxidation of C₂H₄ with O₂ to CO_x, and the reaction of NO₂ with C₂H₄, remain unclear at present. Elucidation of each surface property relevant to each reaction would allow the design of an efficient catalyst by controlling the surface properties to promote the surface oxidation of NO, and the reaction of NO₂ with C₂H₄, but suppress the oxidation of C₂H₄ with O₂.

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要 旨

エチレンによる NO 選択還元反応における金属酸化物触媒の活性

岡崎 文保, 佐々木 猛, 加藤 芳樹, 多田 旭男

北見工業大学化学システム工学科, 090-8507 北海道北見市公園町 165 番地

酸素過剰雰囲気下におけるエチレンを還元剤に用いた NO 選択還元反応と, その反応に活性な触媒の特徴を明らかにする関連反応 ($\text{NO} + \text{O}_2$ 反応, $\text{C}_2\text{H}_4 + \text{O}_2$ 反応, $\text{NO}_2 + \text{C}_2\text{H}_4$ 反応および $\text{NO} + \text{C}_2\text{H}_4$ 反応) について, 金属酸化物 13 種類の触媒活性を調べた。13 種類の金属酸化物の中で, アルミナは NO 選択還元反応に最も高い活性を示した。続いて ZrO_2 , SnO_2 , MgO , CaO , Y_2O_3 および TiO_2 が活性を示し, WO_3 , Co_3O_4 , CuO , Fe_2O_3 , ZnO および SiO_2 は活性をほとんど示さなかった。アル

ミナを含む NO 選択還元反応に活性な触媒は, $\text{NO} + \text{O}_2$ 反応および N_2 を生成する $\text{NO}_2 + \text{C}_2\text{H}_4$ 反応の両方に高い活性を示し, $\text{C}_2\text{H}_4 + \text{O}_2$ 反応に低活性であるという特徴があった。一方, Co_3O_4 , CuO および Fe_2O_3 は $\text{NO} + \text{O}_2$ 反応に高い活性を示したが, $\text{C}_2\text{H}_4 + \text{O}_2$ 反応にも高活性であるため, C_2H_4 は NO の還元に参加しないで消費される。活性な触媒が有する特徴は, NO から NO_2 への酸化とそれに続く NO_2 の C_2H_4 による還元によって N_2 を生成する NO 選択還元反応の反応スキームを支持する。

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