An $^{18}O_2$ Temperature-Programmed Isotope Exchange Study of Transition-Metal-Containing ZSM-5 Zeolites Used for Oxydehydrogenation of Ethane

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The oxydehydrogenation of ethane was studied over a number of transition-metal-containing ZSM-5 catalysts, e.g., Co–H–ZSM-5, Cu–Na–ZSM-5, Nb–ZSM-5, and V–ZSM-5. It has been shown that the introduction of transition metal cations into ZSM-5 zeolite, either as charge balancing cations (Co^{2+}, Nb^{5+}) or as lattice cation (V^{5+}), enhances the activity and selectivity of the catalysts for the oxydehydrogenation of ethane. The $^{18}O_2$ temperature-programmed isotope exchange technique was used to probe the likely active sites on the catalysts. It was demonstrated that the introduction of transition metal cations results in the formation of active sites responsible for the formation of single-step double exchange between gas phase oxygen and lattice oxygen. The activity for formation of single-step double exchange $^{16}O_2$ is a good indicator for the activity for oxydehydrogenation of ethane to form ethylene. The introduction of transition metal cations (Cu^{2+}, Co^{2+}, etc.) into ZSM-5 zeolite lowers the temperature required for isotope exchange between gas phase oxygen and lattice oxygen. The temperature required for isotope exchange depends on the cations introduced. The activity for facilitating single-step double exchange between gas phase $^{18}O_2$ and lattice oxygen (^{16}O) and the activity for oxydehydrogenation of ethane to ethylene decrease in the same order: Co–H–ZSM-5 > Cu–Na–ZSM-5 > [V]–ZSM-5 > Nb–ZSM-5 > Na–ZSM-5 ~ H–ZSM-5 ~Cu–ZSM-5. It appears that the structural defects created by introducing transition metal cations are responsible for the enhanced activity and selectivity for the oxydehydrogenation of ethane. NH_3-TPD results show that the presence of strong Brønsted acid sites are undesired for oxydehydrogenation reactions. However, the presence of relatively weaker acid sites is not harmful for the reaction. © 1995 Academic Press, Inc.

INTRODUCTION

Zeolites are well-defined microporous crystalline materials. In the past 2 decades or so, their properties as solid acids have been extensively studied (1). However, their redox properties have rarely been explored, though, in principle, they can be readily modified to catalyze oxidation reactions by the introduction of transition metals. Transition metals can be introduced into different zeolite structures and in different oxidation states and coordinations, either as charge neutralizing cations, supported metal clusters, complexes, or lattice cations. Therefore, by tuning the state, the location, and the concentration of transition metal cations or a combination of more than one type of cation, we may be able to produce catalysts with better performance for the oxydehydrogenation of ethane.

In this work, Co^{2+}–, Fe^{3+}–, Cu^{2+}–, Cu^+–ZSM-5, prepared by ion-exchange, [V]–ZSM-5 prepared by isomorphic substitution, and Nb–ZSM-5 prepared by impregnation were studied for the oxydehydrogenation of ethane. The choice of transition metals was directed toward lowering the reaction temperatures required for the oxydehydrogenation of ethane and toward higher selectivity to hydrocarbon products. To elucidate the effect of zeolite acidity on product selectivity, both acid form (H–ZSM-5) and neutral form ([V]–ZSM-5, Na–ZSM-5) ZSM-5 were used for preparing transition-metal-containing ZSM-5 catalysts.

$^{18}O_2$-TPIE (temperature-programmed isotope exchange) was employed to determine the degree of isotope exchange between gas phase oxygen and zeolite lattice oxygen and the type of isotope species formed (i.e., $^{16}O^{18}O$, $^{16}O^{16}O$). This technique was previously used for the study of oxide catalysts employed in the oxidative coupling of methane, e.g., Sr/La_2O_3 (2), and Li/MgO and Ca–Ni–K oxide (3). The latter work demonstrated that there are two different types of active sites present on both Li/MgO and Ca–Ni–K oxide catalysts and it was concluded that these sites enable the single-step double exchange between gas phase oxygen and lattice oxygen responsible for their activity for oxidative coupling of methane at relatively low temperatures (≤600°C). The present work again proved that $^{18}O_2$ temperature programmed isotope exchange (TPIE) is a very powerful

technique in determining the probable active sites created by the introduction of transition metals into ZSM-5 zeolite for the oxydehydrogenation of ethane. In conjunction with NH_3-TPD results, the role of strong Brønsted acid sites and that of structural defects created by introducing transition metal cations in the oxydehydrogenation reactions were studied.

EXPERIMENTAL

Materials

Zeolite H–ZSM-5 and Na–ZSM-5 were prepared and characterized by the standard method (4), giving a sample with a SiO_2/Al_2O_3 molar ratio of 59/1. The ZSM-5 consisted of hexagonally terminated lath-like crystals (average size ca. 2 μm) associated into agglomerates, as shown by scanning electron microscopy.

Dy–H–ZSM-5, Fe–H–ZSM-5, and Cr–H–ZSM-5 were prepared by ion exchange of H–ZSM-5 with their corresponding 1.0 M nitrate aqueous solution at room temperature. Co–HZSM-5 and Co–Na–ZSM-5 were prepared by refluxing H–ZSM-5 and Na–ZSM-5 zeolites, respectively, with 0.5 M $Co(NO_3)_2$ (AR grade, May & Baker) aqueous solution at a ratio of 10 g zeolite/300 cm^3 solution for 20 h. The samples were thoroughly washed with distilled water and dried at 110°C overnight.

Ru–Na–ZSM-5 was prepared by an ion exchange technique. A Ru^{3+}-containing aqueous solution was freshly prepared by dissolving 1.0 g of $Ru(NH_3)_6Cl_3$ (99.9%, Johnson Matthey) in 20 g of distilled water and 10 g of Na–ZSM-5 zeolite was added to the Ru^{3+}-containing solution. The mixture was heated under refluxing conditions and with constant stirring. The exchange lasted for 20 h. A dark purple powder material was obtained after filtration, washing, and drying under vacuum.

[V]–ZSM-5 was prepared by using an isomorphic substitution technique. H–ZSM-5 zeolite was treated with $VOCl_3$ (AR grade, Aldrich) by gas–solid state reaction at 520°C. The preparation procedure was described previously (5). XRD examination gave no evidence of structural change of the H–ZSM-5 as a result of the treatment. XPS examination of [V]–ZSM-5 showed that most of the introduced vanadium remains as V^{5+} (ca. 93%) with a small fraction of V^{4+} species (ca. 7%) which was believed to be formed by the reduction of V^{5+} by HCl, as suggested by Whittington and Anderson (6).

Nb-containing ZSM-5 zeolite catalysts were prepared by impregnating H–ZSM-5 or Na–ZSM-5 with a freshly prepared aqueous solution of niobium oxalate. The latter was prepared from niobium pentachloride ($\geq$99%, Johnson Matthey) and oxalic acid (reagent grade, Aldrich). The mixture was dried at 110°C before being calcined at 500°C for 20 h.

The concentration of transition metal cations of the

samples was measured by atomic absorption spectroscopy. The number of Brønsted acid sites of the samples was determined by exhaustive ion exchange with 1.0 M $NaNO_3$ solution at room temperature and subsequent titration of the liberated protons with 0.05 M sodium hydroxide solution.

$^{18}O_2$ gas used for TPIE experiments was from Icon ($^{18}O_2$ purity: $\geq$99.5% atomic).

NH_3 (anhydrous) was from Matheson.

Reactions and Product Analysis

Reactions of ethane with oxygen were carried out in a fixed bed tubular quartz reactor (i.d., 5 mm). The postcatalyst bed section of the reactor was filled with quartz chips to reduce the postreaction dead volume. The ethane to oxygen ratio was 2/1. With a catalyst loading of 0.25 g, the flow rates of ethane and oxygen were 6 and 3 cm$^3 \cdot$ min^{-1}, respectively. Reactor effluents were analyzed by on-line gas chromatography (Hewlett-Packard 5890A; Carbon Sieve IIS column/TCD detector and Porapak-Q column/FID detector). The water produced was removed by a cold trap positioned between the outlet of the reactor and the inlet of the sampling valve.

$^{18}O_2$-TPIE

The temperature-programmed isotope exchange (TPIE) experiments were carried out in a tubular quartz reactor (i.d., 3.6 mm). The amount of catalyst used was 50 mg unless stated otherwise. To avoid possible interference from preadsorbed oxygen and water, the catalysts were treated in high purity helium (99.999%, Alfagaz) at 550°C for at least 2 h and then cooled to 30°C before TPIE was carried out. The flow rate of helium was 100 cm$^3 \cdot$ min^{-1}. In the TPIE experiments, the flow rate of $^{18}O_2$ was 1 cm$^3 \cdot$ min^{-1}. The carrier (high purity helium) flow rate was 50 cm$^3 \cdot$ min^{-1}. The TPIE started at 30°C and the heating rate was 10°C $\cdot$ min^{-1} to 700°C. The gas effluents were analyzed by a Hewlett–Packard 5971A quadrupole mass spectrometer. The interface used between the outlet of the reactor and the inlet of the mass selective detector was described elsewhere (3).

NH_3-TPD

The experimental setup used in NH_3 temperature-programmed desorption (TPD) experiments was the same as that used in $^{18}O_2$-TPIE experiments. Adsorption of ammonia on catalyst was carried out at 30°C. The gas mixture consisted of ammonia and helium. Their corresponding flow rates were 10 and 50 cm$^3 \cdot$ min^{-1}. The amount of catalyst used was 50 mg. The adsorption experiment lasted for 40 min and then the sample was purged with helium (50 cm$^3 \cdot$ min^{-1}) until the level of ammonia in the effluent dropped to background level before temperature-pro-

TABLE 1

Composition and Other Properties of ZSM-5 Zeolite Catalysts

Catalyst	Acidity [H$^+$] (mmol·g^{-1})	Metal cation (mmol·g^{-1})	BET surface area (m^2·g^{-1})	Pore volume (cm^3·g^{-1})
H–ZSM-5	0.52	0	324	0.15
Na–ZSM-5	0.02	0.50	342	0.14
Nb–Na–ZSM-5	0.03	0.25	319	0.14
Co–H–ZSM-5	0.38	0.06	332	0.15
[V]–ZSM-5	0	0.45	—	—
Ru–Na–ZSM-5	0	0.10	317	0.14
Cu–Na–ZSM-5	0	0.17	336	0.14

grammed desorption was started. The TPD started at 30°C at a heating rate of 10°C · min^{-1} to 700°C. Again, the effluent gas was monitored by a quadrupole mass spectrometer.

RESULTS

The acidity, composition, and BET surface area of some of the catalysts studied are given in Table 1. Except for the H–ZSM-5 and Co–HZSM-5 catalysts, the amounts of Na$^+$ exchangeable protons present in other ZSM-5 catalysts are negligible, suggesting that most of the Brønsted acid sites have been removed by exchange with Na$^+$ or by isomorphic substitution in the case of [V]–ZSM-5. The BET surface area and micropore volume data were obtained from nitrogen adsorption isotherm measured at 77 K and the results were analyzed by the α_s-plot method using nonporous hydroxylated silica as standard (7). In the α_s plot, from the region which gave consistent linear lines, lines of best fit were calculated. The slope and intercept were used to determine the external surface area and the micropore volume, respectively. The total surface area and micropore volume results in Table 1 show that introduction of the cations does not cause any significant change in total surface area or micropore volume, suggesting that no pore blocking or plugging occurred as a result of ion exchange treatment. Our XRD results showed that no detectable amounts of extra phases were formed after the ion exchange treatment, indicating that all the resulting catalysts maintained the ZSM-5 crystal phase. We believe that all the transition metal cations introduced by ion exchange were in the countercation positions; however, we do not have surface analysis data to rule out the possibility of formation of transition metal oxide clusters which might locate outside the micropores of ZSM-5 zeolite.

The results of the reaction of ethane with oxygen over various ZSM-5 catalysts at 400°C are given in Table 2. All data presented in the table were obtained after 2 h time on stream. In all cases, no significant deactivation

was observed. However, minor coke deposition was noticed after longer runs (>12 h).

$^{18}O_2$-TPIE results are presented in Table 3. It gives the amounts of single exchange ($^{16}O^{18}O$) and double exchange ($^{16}O^{16}O$) oxygens formed during the temperature programming and the minimal temperature required for isotope exchange to occur.

Table 4 summarizes NH$_3$-TPD results. It includes the total amount of ammonia adsorbed and acid strength distribution (listed as the temperatures corresponding to major desorption peaks).

Table 5 presents the activity data for ethylene formation from ethane oxydehydrogenation and isotope exchange between gas phase $^{18}O_2$ and lattice oxygen on Co–, Cu–, [V]–, Nb–, Na–, and H–ZSM-5 zeolite catalysts.

The TPIE profiles of single exchange oxygen ($^{16}O^{18}O$) and double exchange oxygen ($^{16}O^{16}O$) for H–ZSM-5, Co–H–ZSM-5, and Cu–Na–ZSM-5 zeolites are given in Figs. 1, 2, and 3, respectively.

DISCUSSION

Catalytic Performance

The data presented in Table 2 show that the activity of catalysts in facilitating the reaction of ethane with oxygen decreases in the order: Ru^{III}–Na–ZSM-5 > Cu^{II}–Na–ZSM-5 ~ Cu^I–H–ZSM-5 > Co^{II}–Na–ZSM-5 > V^V–Na–ZSM-5 ~ H–ZSM-5 ~ Co^{II}–H–ZSM-5 > Cr^{III}–H–ZSM-5 ~ Fe^{III}–H–ZSM-5 > Dy–H–ZSM-5 ~ Na–ZSM-5.

From the data in Table 2, it is clear that the performance of the catalysts is governed by the nature of the metal cations and the acidity of the parent zeolite precursor.

H–ZSM-5 zeolite is much more active than Na–ZSM-5 (conversion of ethane: 4.3% vs 0.6%), but is significantly less selective for the oxydehydrogenation of ethane (selectivity to hydrocarbons: 3% vs 36%). In addition, there is more methane produced over H–ZSM-5 than over Na–ZSM-5. These data suggest that the strong Brønsted acid sites of H–ZSM-5 are capable of activating oxygen and facilitating reactions between ethane and oxygen leading almost exclusively to the formation of carbon dioxide and resulting in the formation of more cracking products. This is in agreement with previous studies of oxydehydrogenation of ethane and propane (5, 8) where it was concluded that strong Brønsted acid sites are responsible for unselective oxidation to carbon oxides and for cracking activity. Removal of strong Brønsted acid sites by Na$^+$ ion exchange results in much lower activity but improves selectivity to hydrocarbons. Thus, strong Brønsted acid sites are undesirable for the oxydehydrogenation of ethane.

For Ru–Na–ZSM-5, the selectivity to hydrocarbons is quite high compared to other catalysts studied; however,

TABLE 2

Reaction of Ethane with Oxygen over Zeolite Based Catalysts at 400°C[a]

Catalyst	Conversion (mol%)		Selectivity % (mol%)			
	C_2H_6	O_2	CH_4	CO	CO_2	HC[b]
Co–H–ZSM-5	3.4	31	0.8	15	38	47
Co–Na–ZSM-5	8.0	57	4.0	1	80	19
Cu^I–H–ZSM-5	14	95	0.1	4	85	11
Cr^{III}–H–ZSM-5	2.6	36	0.6	52	28	20
Nb–Na–ZSM-5[c]	2.0	25	1	18	46	35
Fe–H–ZSM-5	2.1	33	0.7	7	78	15
Dy–H–ZSM-5	0.9	27	1.4	25	53	22
H–ZSM-5	4.3	31	1.6	12	85	3
Ru–Na–ZSM-5[d]	20.0	86	36	14	49	37
Cu^{II}–Na–ZSM-5[e]	16	91	0.5	9	84	7
V–Na–ZSM-5	4.6	23	0.6	1	72	27
Na–ZSM-5	0.6	6.5	1.5	10	54	36

[a] Catalyst, 0.25g; ethane, 6 cm$^3 \cdot$ min^{-1}; oxygen, 3 cm$^3 \cdot$ min^{-1}.
[b] HC, C_{2+} hydrocarbon products.
[c] Data obtained at 450°C.
[d] Ru, 1 wt%.
[e] Reaction at 350°C.

its exclusive generation of methane makes it a bad catalyst for the oxydehydrogenation of ethane to produce ethylene.

Both Cu^I–H–ZSM-5 and Cu^{II}–Na–ZSM-5 catalysts are very active for the reaction of ethane with oxygen, but their selectivities to hydrocarbons are very low. For both catalysts, carbon dioxide is the predominant product. Thus, they are excellent oxidation catalysts but not for the oxydehydrogenation of ethane.

The behavior of Co^{2+}–Na–ZSM-5 is similar to that of Cu^{2+}–Na–ZSM-5, except that it has higher cracking activity.

In terms of activity, Co–H–ZSM-5 is less active than Co–NaZSM-5 for the reaction of ethane with oxygen. However, Co–H–ZSM-5 gives much higher selectivity to hydrocarbon products than Co–Na–ZSM-5 (47% vs 19%); moreover, it also generates less cracking product.

This difference cannot be explained by differences in acidity because normally acid ZSM-5 has much higher activity toward complete oxidation and higher tendency for cracking leading to the formation of methane, which means that Co–H–ZSM-5 should have lower selectivity

TABLE 3

Availability of Lattice Oxygen Determined by $^{18}O_2$-TPIE[a]

Catalyst	Lattice oxygen exchanged %		Temperature required for isotope exchange (°C)
	$^{16}O^{18}O$	$^{16}O^{16}O$	
Cu–Na–ZSM-5	6.9	1.1	240
Nb–Na–ZSM-5	5.1	0.4	360
[V]–ZSM-5	1.1	0.1	340
Co–H–ZSM-5	0.7	0.3	400
H–ZSM-5	0.4	0	450
Na–ZSM-5	0.3	0	400

[a] Catalyst, 50 mg; 2 vol% of $^{18}O_2$ in 50 cm$^3 \cdot$ min^{-1} helium; from 30 to 700°C at 10°C $\cdot$ min^{-1}.

TABLE 4

Acidity and Acid Strength of ZSM-5 Based Catalysts Determined by NH_3-TPD[a]

Catalyst	NH_3 adsorbed (mmol $\cdot$ g^{-1})	Temperatures of major TPD peaks[b] (°C)
H–ZSM-5	8.5	160 (vs), 260 (s), 400 (m), 480 (m)
Co–H–ZSM-5	3.1	160 (vs), 260 (w), 400 (m)
Nb–Na–ZSM-5	17.0[c]	160 (s), 260 (m), 360 (m)
Na–ZSM-5	1.0	140 (s), 270 (m)
NaN_3/Na–ZSM-5[d]	0	—
[V]–ZSM-5	0	—

[a] Catalyst, 50 mg; Helium 50 cm$^3 \cdot$ min^{-1}; 30 to 700°C at 10°C $\cdot$ min^{-1}.
[b] Peak intensity, vs, very strong; s, strong; m, medium; w, weak.
[c] Due to the presence of excess of niobium oxalate.
[d] Na–ZSM-5 treated with sodium azide.

TABLE 5

Activities for Oxydehydrogenation of Ethane to Ethylene and Formation of Doubly Exchanged Oxygen of Different ZSM-5 Zeolite Catalysts

Catalyst	Rate of formation of $^{16}O_2$ from exchange of lattice oxygen with gas phase $^{18}O_2$ at 400°C $\times 10^5$ ($^{16}O_2$ molecules $\cdot$ s^{-1} $\cdot$ site^{-1})[a]	Rate of formation of ethylene from oxydehydrogenation of ethane at 400°C $\times 10^3$ (C_2H_4 molecules $\cdot$ s^{-1} $\cdot$ site^{-1})
Co–H–ZSM-5	4.85	3.63
Cu–Na–ZSM-5	2.25[b]	0.88[b]
[V]–ZSM-5	1.27	0.38
Nb–NaZSM-5	1.01	0.38
Na–ZSM-5	<0.01	0.06
H–ZSM-5	<0.01	0.03

[a] For Co–, Cu–, [V]–, and Nb–ZSM-5, the number of transition metal sites introduced were used, while for Na–ZSM-5 and H–ZSM-5, Na cation and proton were assumed as active sites.

[b] At 350°C.

toward hydrocarbon products and higher selectivity to methane (by cracking) if acidity were to play a predominant role in determining product distribution. The levels of Co^{2+} loading of Co–H–ZSM-5 and Co–Na–ZSM-5 are very close. Thus, the difference being caused by different cobalt loadings may be ruled out. Therefore, the observed difference in selectivity to hydrocarbons is the result of a combination of the effects of transition metal cation Co^{2+} and acidity. It appears that moderate acidity of ZSM-5 is needed for high selectivity to hydrocarbons.

V–Na–ZSM-5 is slightly more active than Co–H–ZSM-5 but less selective, making it not superior to Co–H–ZSM-5 for oxydehydrogenation of ethane. Nb–Na–ZSM-5 is

less active than Co–H–ZSM-5. Its selectivity (35%) is the second highest among the ZSM-5 zeolite catalysts studied.

Cr^{3+}-, Fe^{3+}-, and Dy^{3+}-exchanged H–ZSM-5 catalysts behave similarly in the oxydehydrogenation of ethane. Their selectivities to hydrocarbons are reasonably high. Dy-H–ZSM-5 is the least active among the three and it produces the highest level of methane.

In summary, Cu^{2+}- and Cu^+- exchanged ZSM-5 are the most active catalysts for complete oxidation. H–ZSM-5 is also a good catalyst for oxidation of ethane. Co–H–ZSM-5 is the best catalyst for the oxydehydrogen-
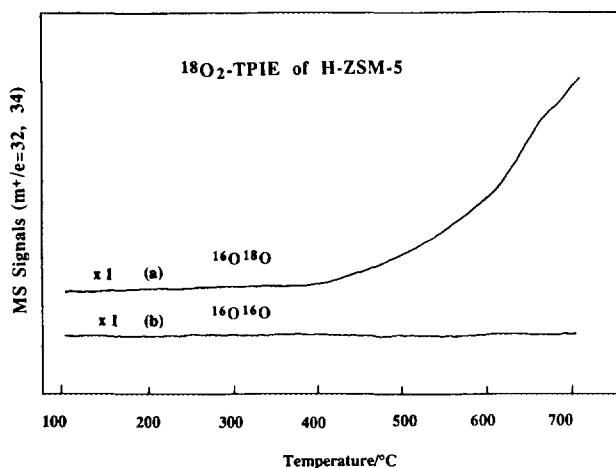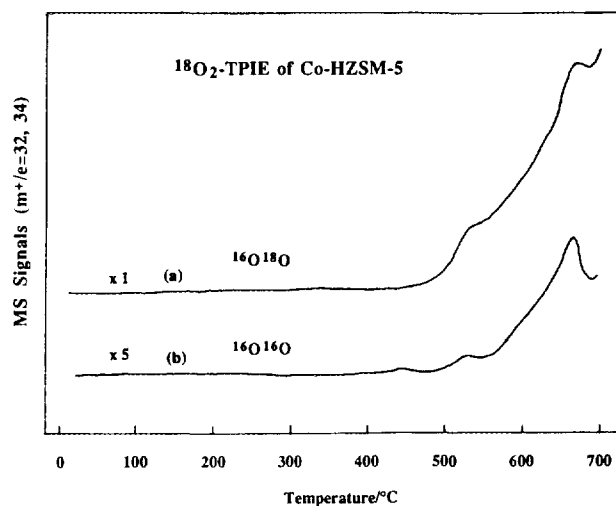

FIG. 1. Temperature-programmed exchange of lattice oxygen in H–ZSM-5 zeolite by gas phase oxygen ($^{18}O_2$): (a) $^{16}O^{18}O$; (b) $^{16}O^{16}O$ (catalyst, 50 mg; $^{18}O_2$: 1 cm^3 $\cdot$ min^{-1}; He, 50 cm^3 $\cdot$ min^{-1}; 30 to 700°C at 10°C $\cdot$ min^{-1}).
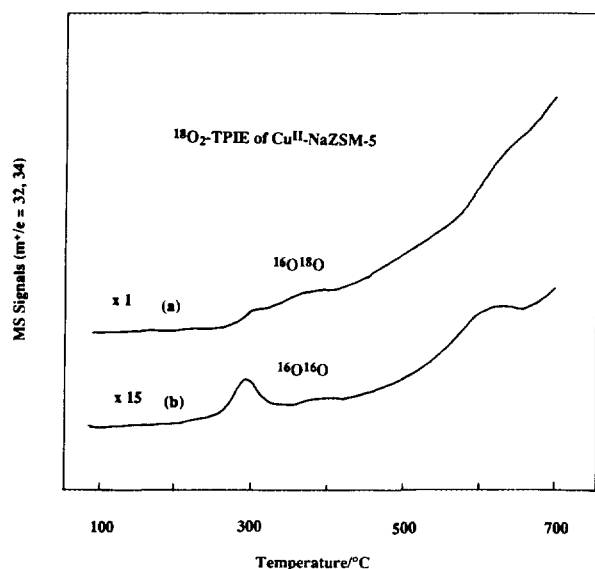

FIG. 2. Temperature-programmed exchange of lattice oxygen in Co–H–ZSM-5 zeolite by gas phase oxygen ($^{18}O_2$): (a) $^{16}O^{18}O$; (b) $^{16}O^{16}O$ (catalyst, 50 mg; $^{18}O_2$: 1 cm^3 $\cdot$ min^{-1}; He, 50 cm^3 $\cdot$ min^{-1}; 30 to 700°C at 10°C $\cdot$ min^{-1}).

FIG. 3. Temperature-programmed exchange of lattice oxygen in Cu–Na–ZSM-5 zeolite by gas phase oxygen (^{18}O$_2$): (a) ^{16}O^{18}O; (b) ^{16}O^{16}O (catalyst, 50 mg; ^{18}O$_2$: 1 cm$^3 \cdot$ min^{-1}; He, 50 cm$^3 \cdot$ min^{-1}; 30 to 700°C at 10°C $\cdot$ min^{-1}).

ation of ethane. Na–ZSM-5 is the least active of the catalysts studied. Thus, despite its fairly high selectivity to hydrocarbons, Na–ZSM-5 is not an ideal candidate for the oxydehydrogenation of ethane. Cr–H–ZSM-5, Fe–H–ZSM-5, and Dy–H–ZSM-5 are neither more active nor more selective than Co–H–ZSM-5. Therefore, Co–H–ZSM-5 gives the best performance of the catalyst tested for the oxydehydrogenation of ethane.

^{18}O$_2$-TPIE Study

Isotope exchange between gas phase oxygen and lattice oxygen of ZSM-5 zeolites occurs at temperatures above 240°C depending on the nature of cations present. The amount of lattice oxygen exchanged (see Table 3) is determined by the cation present. Except for H–ZSM-5 and Na–ZSM-5 zeolite, all the other catalysts exhibit two types of isotope exchange species (singly exchanged ^{16}O^{18}O and doubly exchanged ^{16}O^{16}O).

The isotope exchange observed in the present study is solely due to the exchange between gas phase oxygen and lattice oxygen, or so-called heterophase exchange because blank experiments (in the absence of catalyst) showed no isotope exchange occurring in the temperature range (30 to 700°C) used in the present study. In addition, the TPD experiments carried out on catalysts pretreated at 550°C in helium showed no evolution of oxygen, suggesting that the ^{16}O^{16}O species observed in this study was formed by either consecutive exchange of gas phase oxygen (^{18}O$_2$) with lattice oxygen (^{16}O) or single step multiple exchange.

Chemisorbed oxygen was observed on Na–Y, H–Y, and Cu^{II}Na–Y zeolites by using a temperature-programmed desorption technique (9). It showed that Na–Y and H–Y zeolites do not have significant capacity for the chemisorption of oxygen. Introduction of Cu^{2+} into Y zeolites resulted in the formation of active sites responsible for the chemisorption of oxygen. There were at least two types of active sites present in Cu^{II}–Na–Y zeolite; their corresponding TPD temperatures are ca. 320 and 470°C. The fact that we did not observe desorption of oxygen in our TPD experiments performed after pretreatment at 550°C in helium suggests that any preadsorbed oxygens due to exposure to air (e.g., in storage or transfer) must have desorbed at 550°C.

The TPIE profiles of H–ZSM-5 (Fig. 1) show that there is no formation of doubly exchanged oxygen (^{16}O^{16}O). ^{16}O^{18}O is the only isotope exchange product observed. The isotope exchange takes place at temperatures $\geq$420°C. It appears the extent of exchange (or exchange rate) increases with temperature monotonically.

The TPIE profiles of Na–ZSM-5 are similar to those of H–ZSM-5. There is no doubly exchanged oxygen formed. It seems that the exchange rate between gas phase oxygen and lattice oxygen to form ^{16}O^{18}O increases linearly with temperature.

Figure 2 shows two isotope exchange species formed over Co–H–ZSM-5 zeolite which increase with temperature. The double exchange occurs at temperatures $\geq$360°C while single exchange takes place at higher temperatures ($\geq$460°C). Apart from a weak low-temperature peak of ^{16}O^{16}O at 440°C, the two shoulders centered at 520 and 650°C appear at approximately the same temperatures as those of ^{16}O^{18}O.

For Cu–Na–ZSM-5 (Fig. 3), the formation of doubly exchanged oxygen (^{16}O^{16}O) occurs at temperatures $\geq$200°C, which is about 80°C lower than singly exchanged oxygen (^{16}O^{18}O).

Heterophase isotope exchange between gas phase oxygen (^{18}O$_2$) and lattice oxygen (^{16}O) of zeolite may lead to formation of singly exchanged and doubly exchanged products. It is possible to distinguish two cases: single exchange and multiple exchange based on experimental observations of either the time dependence or the temperature dependence of the isotope distribution of molecular oxygen species ^{16}O^{16}O, ^{16}O^{18}O, and ^{18}O^{18}O. For single exchange, there is only one oxygen atom of the molecule exchanged for one lattice oxygen atom of the catalyst during the residence time on the catalyst surface,

$$^{18}O^{18}O(g) + |^{16}O|_l = {}^{18}O^{16}O(g) + |^{18}O|_l,   (A)$$
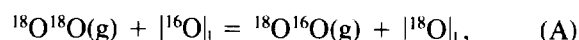
where $|O|_l$ and O$_2$(g) represent lattice oxygen on the catalyst surface and gas phase oxygen, respectively. Likewise, the single-step double exchange involves both oxy-

gen atoms of the gas phase oxygen molecule exchanged for one stay on the catalyst surface for two lattice oxygen atoms,

$$^{18}O^{18}O(g) + 2|^{16}O|_l = {}^{16}O^{16}O(g) + 2|^{18}O|_l. \quad (B)$$
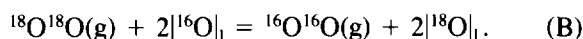
The use of temperature programming during isotope exchange enables one to differentiate whether $^{16}O^{16}O$ formed via a single-step double exchange process or via a two-step consecutive single exchange process. If the doubly exchanged oxygen is formed via the two-step single exchange, there should be at least the same number of doubly exchanged oxygen peaks as there is of singly exchanged oxygen peaks, and more importantly, the temperature at which the secondary exchange occurs is expected to be the same if not higher than that for primary exchange, also, the area under these corresponding peaks should be proportional to that of the singly exchanged peaks because the amount of corresponding secondary exchange product formed should be proportional to the amount of primary exchange product. The fact that the temperature required for the formation of doubly exchanged oxygen was lower than that required for the singly exchanged suggests that the doubly exchanged oxygen was probably solely formed via a single-step multiple exchange process. In conjuction with previous kinetic isotope exchange results on transition metal oxides (10), we conclude that the doubly exchanged oxygen observed in this study is formed by involving two oxygen atoms from the catalyst surface in a single step rather than a two-step single exchange process.

The results presented in Table 3 clearly show that transition-metal-containing ZSM-5 zeolites have a higher capacity for isotope exchange than H–ZSM-5 and Na–ZSM-5. More importantly, on transition-metal-containing ZSM-5 zeolites, the doubly exchanged oxygen species are formed. For these transition-metal-containing ZSM-5 zeolites, the capacity for isotope exchange depends on the cation present. Cu–Na–ZSM-5 has the highest capacity for isotope exchange, followed by Nb–Na–ZSM-5. [V]–ZSM-5 and Co–H–ZSM-5 have similar capacities. They are significantly lower than Cu–Na–ZSM-5 and Nb–Na–ZSM-5. The formation of doubly exchanged oxygen on ZSM-5 zeolites is associated with the introduction of transition metal cations. The ability of transition metal cations in creating active sites responsible for double exchange decreases in the order $Cu^{2+} > Nb^{5+} > Co^{2+} > V^{5+}$. The introduction of transition metal cations into ZSM-5 zeolite not only increases the capacity for isotope exchange but also lowers the temperature required for isotope exchange between gas phase oxygen and lattice oxygen.

The temperature required for isotope exchange to occur depends on the cation introduced. Cu–Na–ZSM-5 (Fig.

3) has the highest capacity for isotope exchange and the lowest temperature required for isotope exchange to occur ($\geq 240°C$ compared to $400°C$ for Na–ZSM-5), suggesting that the high activity of Cu–Na–ZSM-5 for the oxidation of ethane is the result of the high activity of its lattice oxygen at low temperatures. Co–H–ZSM-5 also has a high capacity for double exchange (30% of the total isotope exchange products) and it gives quite high selectivity to hydrocarbons (47%). [V]–ZSM-5 and Cu–Na–ZSM-5 have significantly lower capacity for double isotope exchange, and give lower selectivity to hydrocarbons.

The data presented in Table 3 show that the amounts of lattice oxygen exchanged by gas phase oxygen for both H–ZSM-5 and Na–ZSM-5 are small. If one assumes that only oxygens bridging aluminum and silicon atoms in the ZSM-5 zeolite lattice are exchanged by gas phase oxygen, then the amount of lattice oxygen which can be exchanged is 1.5% of the total lattice oxygen for the ZSM-5 used in this study. The observed values (0.3 and 0.4%) are approximately one quarter of that, implying that not all bridging oxygens are exchanged under the conditions employed.

Von Ballmoos studied the ^{18}O-exchange between $H_2{}^{18}O$ (or $D_2{}^{18}O$) and framework oxygen (^{16}O) of various zeolites (11). It was found that the extent of isotope exchange depends strongly on the exchange temperature and media (e.g., in the presence of acids). At temperatures $\leq 95°C$, exchange appears to occur exclusively at oxygen sites bridging silicon and aluminum atoms, that is, the number of lattice oxygen exchanged roughly equals the number of framework aluminum sites. At temperatures $\geq 100°C$, isotope exchanges are no longer limited to Al–O–Si, and exchanges with Si–O–Si also take place. The higher the exchange temperature, the higher the degree of isotope exchange. Exchange between $H_2{}^{18}O$ and H–ZSM-5 at $600°C$ for 1 h resulted in exchange of 70% of the lattice oxygen (11). This is in sharp contrast to our $^{18}O_2/H–$, Na–ZSM-5 TPIE results, which indicate that there is only 0.3~0.4% lattice oxygen exchanged at temperatures up to $700°C$. This difference may be interpreted by the fact that the nonpolar $^{18}O_2$ molecules are much weaker reagents in attacking the zeolite framework than the highly polar $H_2{}^{18}O$ molecules. The low activity of zeolites toward isotope exchange of O_2 was also observed by others (12). They found that transition metal containing ZSM-5 zeolites have much lower activity toward isotope exchange with gas phase oxygen than their oxides. For instance, the exchange rate on [Fe]–ZSM-5 was found to be two orders of magnitude lower than that over Fe_2O_3 (13). The isotope exchange between gas phase oxygen and lattice oxygen of H–ZSM-5 doped with iron requires temperatures $\geq 500°C$ (12).

The decrease in temperature required for isotope exchange between gas phase oxygen and zeolite lattice oxy-

gen by introducing transition metal cations into ZSM-5 is in agreement with previous findings on transition metal containing Na–Y zeolites (14). Panov *et al.* (13) found that introduction of transition metal cations (Cu^{2+}, Ni^{2+}) into Na–Y zeolites led to a significant decrease in exchange temperature (from ~670°C for Na–Y to ≤450°C for Cu–Na–Y, and 570°C for Ni–NaY). In another study by Sobolev *et al.* (15) on the isotope exchange between gas phase oxygen and lattice oxygen of [Fe]–ZSM-5, it was found that the isotope exchange started at temperatures ≤470°C.

Based on the $^{18}O_2$-TPIE results obtained with ZSM-5 zeolites in the present study and the data obtained with Y zeolites and erionite (ERI) zeolite by others (14), it seems that the lattice oxygen possesses higher mobility in Na–ERI and Na–ZSM-5 (and H–ZSM-5 as well) than in Na–Y zeolite. The isotope exchange rates at 700°C are Na–ERI: 61.6×10^{17} atom·g^{-1}·min^{-1} (14), Na–ZSM-5: 46.5×10^{17} atom·g^{-1}·min^{-1}, and Na–Y 8.7×10^{17} atom·g^{-1}·min^{-1} (14). The corresponding pore sizes of Na–ERI, Na–ZSM-5, and Na–Y zeolites are 3.6×5.1 Å (8-member ring); 5.2×5.6 Å (10-member ring), and 7.6×7.8 Å (12-member ring). It appears that the smaller the pore opening of the three-dimensional pore structure, the more lattice oxygen is exchanged by gas phase oxygen. The differences in activity toward isotope exchange cannot be explained by the number of oxygens bridging aluminum and silicon atoms present in the lattice because Na–Y zeolite has the highest (2.5×10^{21} atom·g^{-1}) (14), followed by Na–ERI (2.0×10^{21} atom·g^{-1}) (14), and Na–ZSM-5 has the lowest (3.0×10^{19} atom·g^{-1}). The difference is probably due to structural variations, most likely the size of the pore openings. If one compares the van der Waals diameter of an oxygen molecule (2.9 Å) and the pore size of the three zeolites studied, one will find that they all are large enough to allow oxygen molecules to pass. However, the interaction between a gas phase oxygen molecules with the lattice oxygen of Na–ERI and Na–ZSM-5 zeolites is expected to be stronger than with the lattice oxygen of Na–Y when oxygen molecules pass through the pore channels. It may be this interaction that is responsible for the much higher rate of isotope exchange between gas phase oxygen and lattice oxygen on Na–ERI and Na–ZSM-5 zeolites than on Na–Y zeolite.

It has been suggested (16) that for transition metal oxides isotope exchanges between gas phase oxygen and lattice oxygen involving two oxygen atoms from surface oxide predominate. Such an exchange occurs by virtue of dissociative adsorption of dioxygen followed by desorption of molecules with modified isotope composition. If the surface atoms mix rapidly enough, the isotope composition of desorbed molecules corresponds to the ratio of the surface concentrations of isotopes.

In the case of ZSM-5 zeolite, all its lattice oxygens

bridging framework aluminum and silicon atoms may be treated as surface oxygens because they all are accessible to incoming molecules. Thus the difference in isotope exchange with gas phase oxygen between transition metal containing ZSM-5 and H–ZSM-5 or Na–ZSM-5 is caused by the presence of transition metal cations in the zeolite.

The results in Table 5 show that the activity for the formation of ethylene from oxydehydrogenation of ethane decreases in the order Co–HZSM-5 > Cu–Na–ZSM-5 > [V]–ZSM-5 > Nb–Na–ZSM-5 > Na–ZSM-5 > H–ZSM-5, and the activity for formation of doubly exchanged $^{16}O_2$ from exchange of lattice oxygen (^{16}O) by gas phase $^{18}O_2$ follows the same trend. Therefore, we suggest that the rate of single-step double exchange between gas phase oxygen and lattice oxygen of zeolite-based catalyst is a good indicator of its activity for oxydehydrogenation of ethane to form ethylene. Thus, catalysts having higher activity for single-step double exchange between gas phase oxygen and lattice oxygen give higher activity for oxydehydrogenation of ethane to ethylene.

CONCLUSIONS

Introduction of transition metal cations into ZSM-5 leads to a significant increase in both the capacity for and rate of isotope exchange between gas phase oxygen and lattice oxygen and the formation of active sites responsible for single step double exchange. Capacity increase for isotope exchange and for the creation of active sites for single-step double exchange depends on the cation introduced. Cu^{2+} and Nb^{5+} are more effective than V^{5+} and Co^{2+} in enhancing the overall capacity for isotope exchange while Co^{2+} and Cu^{2+} create more active sites for single-step double exchange than Nb^{5+} and V^{5+}. The introduction of transition metal cations into ZSM-5 zeolite not only enhances their capacity for isotope exchange but also results in a decrease in the temperature required for isotope exchange.

We demonstrated that the capacity for single-step double exchange between gas phase oxygen and lattice oxygen for ZSM-5 zeolite catalysts is a measurement of their activity for oxydehydrogenation of ethane to form ethylene. Catalysts having a higher rate for facilitating single-step double isotope oxygen exchange (e.g., Co–H–ZSM-5 zeolite) give higher activity for oxydehydrogenation of ethane to form ethylene. The activity for formation of single-step double exchange $^{16}O_2$ and the activity for oxydehydrogenation of ethane to ethylene decrease in the order: Co–H–ZSM-5 > Cu–Na–ZSM-5 > [V]–ZSM-5 > Nb–Na–ZSM-5 > Na–ZSM-5 ~ H–ZSM-5.

ACKNOWLEDGMENTS

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