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Dynamic behavior of basic sites of MgO in Tishchenko reaction

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Abstract

Tishchenko reaction of benzaldehyde was carried out over the MgO whose surface O atoms were enriched with ^{18}O to examine whether the surface O atoms of MgO are incorporated into the product and reactant. The surface lattice ^{18}O atoms were incorporated in both the product and reactant. The ^{18}O concentration was significantly higher for the product than for the reactant. In addition, the ^{18}O in the product ester was located not only in the carbonyl group (C=O) but also in the bridging position (C–O–C); ^{18}O exchange between benzaldehyde and MgO surface occurred not only in the adsorption–desorption of benzaldehyde, but also in the dimerization process. The oxygen exchange results in the migration of active sites of coordinative unsaturated site (CUS) over the surface of MgO catalyst during the reaction.

Keywords: Tishchenko reaction; Benzaldehyde; MgO; Base-catalysed reaction; ^{18}O labeled surface

1. Introduction

In the oxidation of hydrocarbons over mixed metal oxides, it is commonly observed that lattice oxygen atoms of the catalysts are incorporated into the products. During oxidation, surface metal-oxygen (M–O) bonds repeat breaking and recombining. As a result, catalyst surfaces are in such a dynamic state that the surfaces are restructuring during the reaction. This is believed to be caused by weak metal-oxygen bond of the oxidation catalysts.

In contrast to the oxidation catalysts, the surface metal-oxygen bonds of the metal oxides exhibiting acidic and basic properties are generally strong. It is believed that the bonds do not break during catalytic reactions undertaken under mild conditions, and that the catalytically active sites remain unchanged after completion of the catalytic cycles. Incorporation of the surface oxygen atoms into the products in acid or base-catalyzed reactions has never been taken into account.

Recently we found that the metal oxides with basic character exchange their surface oxygen atoms with those of adsorbed CO_2 [1]. When ^{18}O-labelled carbon dioxide ($C^{18}O_2$) was adsorbed on MgO and TPD experiment was run, we found evolution of $C^{18}O^{16}O$ in the temperature range 300–400 K and non-labelled $C^{16}O_2$ in the range 400–600 K. The O exchange occurs through bidentate CO_2 adsorbed on acid-base pair site at CUS as shown in Fig. 1. By one O exchange, the acid–base pair sit at CUS shifts one unit. Successive exchange results in a rollover of the adsorbed CO_2 and migration of CUS to some distance. The surface metal-oxygen bonds break even in the low temperature range, and that the adsorbed carbon dioxide rollsover the surface in the higher temperature range. The surface restructuring takes place during adsorption–desorption of carbon dioxide.

It is conceivable that a similar surface restructuring is involved in the reactions of molecules containing oxygen over solid base catalysts. In particular in the base catalyzed reactions of the molecules containing carbonyl group, incorporation of the surface lattice oxygen into the reactant and/or product may be observable. Such incorporation of the surface lattice oxygen into the product and/or reactant would result in the migration of the surface sites over the surface during catalytic reactions.

Tishchenko reaction is a dimerization of an aldehyde forming an ester, and catalyzed by solid base catalysts such as MgO, CaO, and SrO [2–4] under mild conditions of a temperature range 313–353 K.

$$RCHO + RCHO \rightarrow RCH_2OC(=O)R$$

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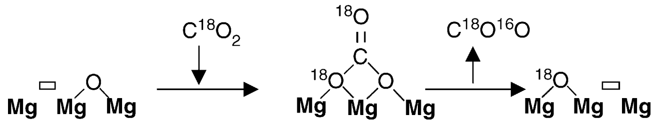


Fig. 1. Oxygen exchange between adsorbed CO_2 and MgO surface □ denotes oxygen vacancy.

Aldehyde possesses carbonyl group and Tishchenko reaction is one of the suitable reactions to explore the dynamics of the surface lattice oxygen. Tishchenko reaction over a metal oxide catalyst is initiated by basic sites and driven by acidic sites. The basic sites are believed to be the oxygen atoms at coordinatively unsaturated sites (CUS) and the acidic sites are metal cations or oxygen vacancies adjacent to the basic sites.

Among Tishchenko reactions, we selected Tishchenko reaction of benzaldehyde to form benzylbenzoate catalyzed by MgO for the reaction to examine behavior of the surface lattice oxygen. The surface of MgO was enriched with ^{18}O and the isotopic distributions in the reactant and product were measured. Tishchenko reaction of benzaldehyde to form benzylbenzoate is shown in Scheme 1.

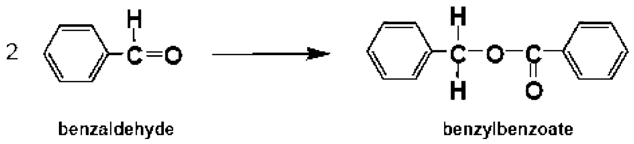
2. Experimental

2.1. Surface enrichment with ^{18}O

The MgO powder (Merck) was soaked in distilled water and once hydrated at ambient temperature for 24 h. After evaporation of the water, the resulting magnesium hydroxide was dried at 373 K for 24 h and used as a precursor of the MgO sample. The magnesium hydroxide precursor was placed in one branch of an H shaped reactor (see Fig. 2) and decomposed in a vacuum at 873 K to obtain the MgO sample (non-labeled MgO). The non-labeled MgO was exposed to ca. 1 Torr of $H_2{}^{18}O$ (^{18}O content 95%, supplied from Nippon Sanso Co.) vapor at room temperature for 1 h to form hydrated MgO. The sample was then heated in a vacuum at 873 K for 30 min to re-convert to oxide. The hydration-decomposition cycle was repeated nine times, and finally the sample was heated in a vacuum at 973 K to obtain a well-exposed oxide surface being enriched with ^{18}O.

2.2. Estimation of surface concentration of ^{18}O

The surface concentration of ^{18}O was determined by means of TPD of adsorbed CO_2. As described earlier, the surface lattice oxygen atoms are exchanged with adsorbed CO_2. Incorporation of the surface lattice oxygen into the desorbed CO_2 increases with the desorption temperature. At first, the fraction of ^{16}O in CO_2 during TPD for $C^{18}O_2$ adsorbed on non-labeled MgO was measured. The obtained fraction was regarded as the standard for 100% ^{16}O-labelled (non-labeled) sample. Then, the fraction of ^{18}O in CO_2 during TPD for $C^{16}O_2$ adsorbed on the ^{18}O-labeled MgO was measured. The surface concentration of ^{18}O in the labeled MgO was estimated by the ratio of the fraction of ^{16}O in CO_2 in the first experiment to the fraction of ^{18}O in CO_2 in the second experiment. The percentage of ^{18}O in the total surface lattice oxygen was calculated to be 92% for the ^{18}O-labeled MgO.



Scheme 1. Tishchenko reaction of benzaldehyde to benzylbenzoate.

2.3. Reaction procedures

The reaction was carried out in an H-shaped glass batch reactor as shown in Fig. 2. One of the two branches was made of quartz. The two branches of the reactor were separated by a breakable seal. ^{18}O-labeled MgO catalyst was prepared in the quartz made branch as described earlier. After the final evacuation of the catalyst at 873 K, the branch was flame-sealed at position (b). Benzaldehyde and benzene (solvent) were purified by passage through 4A molecular sieves and transferred into the other branch kept at liquid nitrogen temperature in a vacuum followed by flame-sealing at position (a). Then, the breakable seal was broken by hitting with the glass bead to transfer the benzaldehyde and benzene stored in the branch by distillation through the broken breakable seal into the branch containing the catalyst kept at liquid nitrogen temperature. Finally, the branch now containing catalyst, reactant and solvent was sealed at position (c) to obtain an I-shaped ampoule. The reaction was started by rapid melting of the reactant at a reaction temperature. The reaction mixture was stirred magnetically. After the reaction, the products were

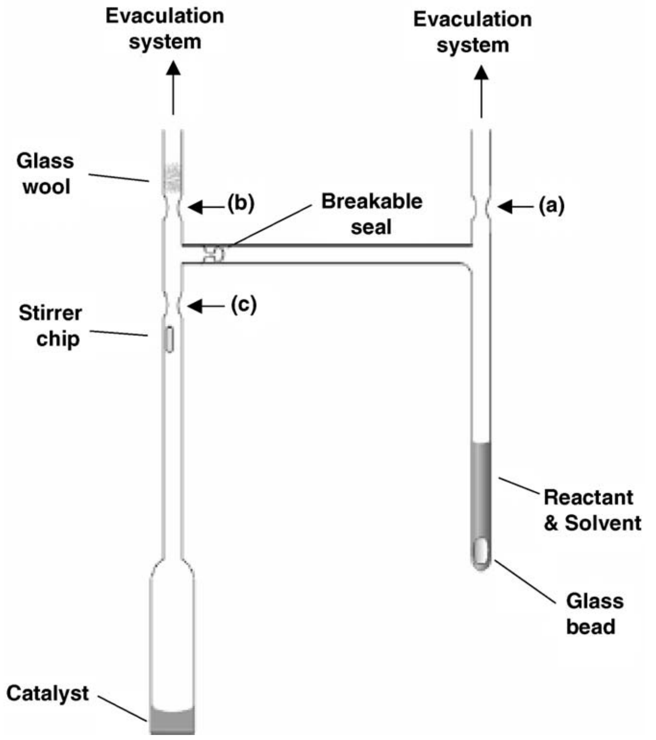


Fig. 2. H-shaped ampoule reactor.

Table 1
Results of Tishchenko reaction of benzaldehyde over ^{18}O-labeled catalyst

Catalyst	^{18}O conc. (%)	React. temp. (K)	React. time (min)	Conv. (%)	Mass peak intensity (%)[a]				
					Benzaldehyde		Benzylbenzoate		
					M	M + 2	M	M + 2	M + 4
Mg^{18}O	92	343	6	46	100	4.1	100	12.5	0.4
Mg^{18}O	92	313	7	7	100	2.2	100	5.7	0.5
Ca^{18}O	88	313	1	9	100	1.8	100	3.9	0.1
Mg^{16}O	0.2[b]	343	3	32	100	0.6	100	1.7	0.1

[a] Determined by GC-MS(EI).

[b] Natural abundance of ^{18}O.

separated from catalyst by filtration and subjected to GC-MS analysis. Electron ionization was employed for mass spectrometric analysis.

3. Results and discussion

In Table 1 are summarized experimental results for the Tishchenko reaction of benzaldehyde over the ^{18}O-labeled MgO at reaction temperatures of 343 and 313 K. The results with non-labeled MgO are also included. In the reaction, only benzylbenzoate was produced; neither benzoic acid nor benzyl alcohol were observed in the analysis by GC. Mass peaks of 108 ($M + 2$) for unconverted benzaldehyde and 214 ($M + 2$) for benzyl benzoate were significantly higher for the reaction over ^{18}O-labeled MgO than over non-labeled MgO. Incorporation of the surface lattice oxygen into both reactant and product took place even at 313 K. The incorporation was more extended at 343 K than at 313 K. The incorporation of the surface oxygen into the reactant and product has never been reported for heterogeneous base-catalyzed reaction under mild reaction conditions.

The incorporation of ^{18}O into benzaldehyde should occur in the similar way as CO_2 exchange with the surface lattice oxygen as depicted in Fig. 1. Carbonyl C of benzaldehyde interacts with the surface O atom adjacent to the coordinatively unsaturated metal cation. The adsorbed benzaldehyde picks up the surface O atom and drops its carbonyl O at the surface O vacancy which is located next to the coordinatively unsaturated metal cation. The incorporation of the surface lattice oxygen into benzaldehyde occurs through adsorption and desorption of benzaldehyde.

In order to examine whether oxygen incorporation is involved in the dimerization step, the percentage of the ester containing ^{18}O was compared to the predicted value. The percentage of the benzaldehyde containing ^{18}O ($M + 2$) after reaction for 6 min at 343 K was 4.1%. In the course of dimerization, the percent isotopic composition of benzaldehyde should be as follows; benzaldehyde containing one ^{18}O (denoted as benzaldehyde-$^{18}o_1$), smaller than 4.1%, and benzaldehyde containing no ^{18}O (denoted as benzaldehyde-$^{18}o_0$), larger than 95.9%. Dimerization of a mixture containing benzaldehyde-$^{18}o_0$ and benzaldehyde-$^{18}o_1$ forms three isotopic benzylbenzoate, benzylbanzoate-$^{18}o_0$, benzylbenzoate-$^{18}o_1$, and benzylbenzoate-$^{18}o_2$. The isotopic composition of benzylbenzoate is as follows if no incorporation of the surface lattice oxygen is involved in the dimerization step;

fraction of benzylbanzoate-$^{18}o_0$ = (fraction of benzaldehyde-$^{18}o_0$)^2
fraction of benzylbanzoate-$^{18}o_1$ = 2 (fraction of benzaldehyde-$^{18}o_0$) × (fraction of benzaldehyde-$^{18}o_1$)
fraction of benzylbanzoate-$^{18}o_2$ = (fraction of benzaldehyde-$^{18}o_1$)^2

Dimerization of a mixture containing 95.9% benzaldehyde-$^{18}o_0$ and 4.1% benzaldehyde-$^{18}o_1$ will form $0.959^2 \times 100\% = 92.0\%$ benzylbenzoate-$^{18}o_0$, 7.8% benzylbenzoate-$^{18}o_1$, and 0.2 benzylbenzoate-$^{18}o_2$.

In the present experiment, the value 7.8% benzylbenzoate-$^{18}o_1$ is the maximum attainable value because the percent isotopic benzaldehyde-$^{18}o_1$ should be lower than 4.1% in the course of reaction till a reaction time of 6 min. The observed value for the percentage of benzylbenzoate-$^{18}o_1$ was 12.5% which is significantly higher than the calculated value 7.8%. Therefore, it is suggested that the dimerization mechanism involves the incorporation of the surface lattice oxygen into the product ester.

It is plausible that the active sites for the reaction are CUS sites such as corner, edge, and kink. The amount of these CUS sites is generally quite small as compared to the total surface oxygen atoms. For instance, the number of corner sites was estimated from hydrogen adsorption to be 6.7×10^{16} sites m^{-2}

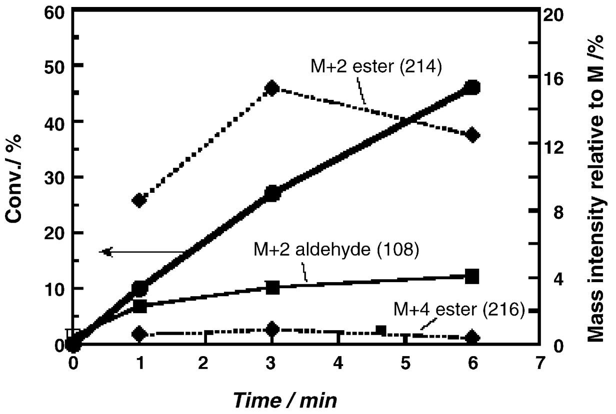


Fig. 3. Time dependence of the incorporation of surface lattice oxygen into the reactant and product.

(ca. 10 mmol site g^{-1}) for MgO [5]. If the exchangeable O atoms were limited to the O atoms located on the original CUS sites, such a small number of sites would have been consumed immediately and substituted by the oxygen (^{16}O) atom of the reactant and product during the reaction. However, the distribution of each ^{18}O-labeled reactant and product did not change drastically with an increase in the conversion as shown in Fig. 3. The amount of the surface lattice oxygen incorporated into the reactant and product was more than 500 mmol g^{-1}, 50 times higher as compared to the corner sites. The surface of MgO is full of the surface lattice oxygen atoms able to be incorporated into the reactant and product. Migration of CUS sites makes the surface lattice oxygen originally distant from CUS sites become exchangeable oxygen.

Before drawing the reaction mechanisms of the Tishchenko reaction of benzaldehyde, it would be important to determine the position of incorporated ^{18}O in the product which possesses two O atoms in a molecule, one in carbonyl (C=O) and the other in C–O–C bonding. The location of ^{18}O is reflected in the fragment peaks in mass spectrum. In an EI-MS spectrometer with hard ionization, alpha-cleavage takes place at the carbonyl position, and the aromatic ester disintegrates predominantly into a fragment with only carbonyl oxygen as shown in Fig. 4. This fragment peak is generally higher than the parent peak. In the case that the ester is partly labeled by ^{18}O, the ratio calculated from the parent mass peaks, 212 (M) and 214 ($M + 2$), gives the labeling content in the whole molecule. The labeling content in the carbonyl position, on the other hand, is obtained from the ratio of the mass peak at 105 and that of 107.

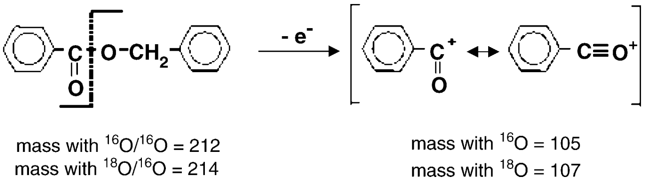


Fig. 4. Fragmentation of benzylbenzoate.

Mass spectrum of the benzylbenzoate produced in the reactions over ^{18}O-labeled MgO at 343 K for 1 min gave the following peak ratios:

peak at 107/peak at 105 = 0.106, peak at 214/peak at 212 = 0.086

while in the reaction over non-labeled MgO at 343 for 1 min gave the following peak ratios:

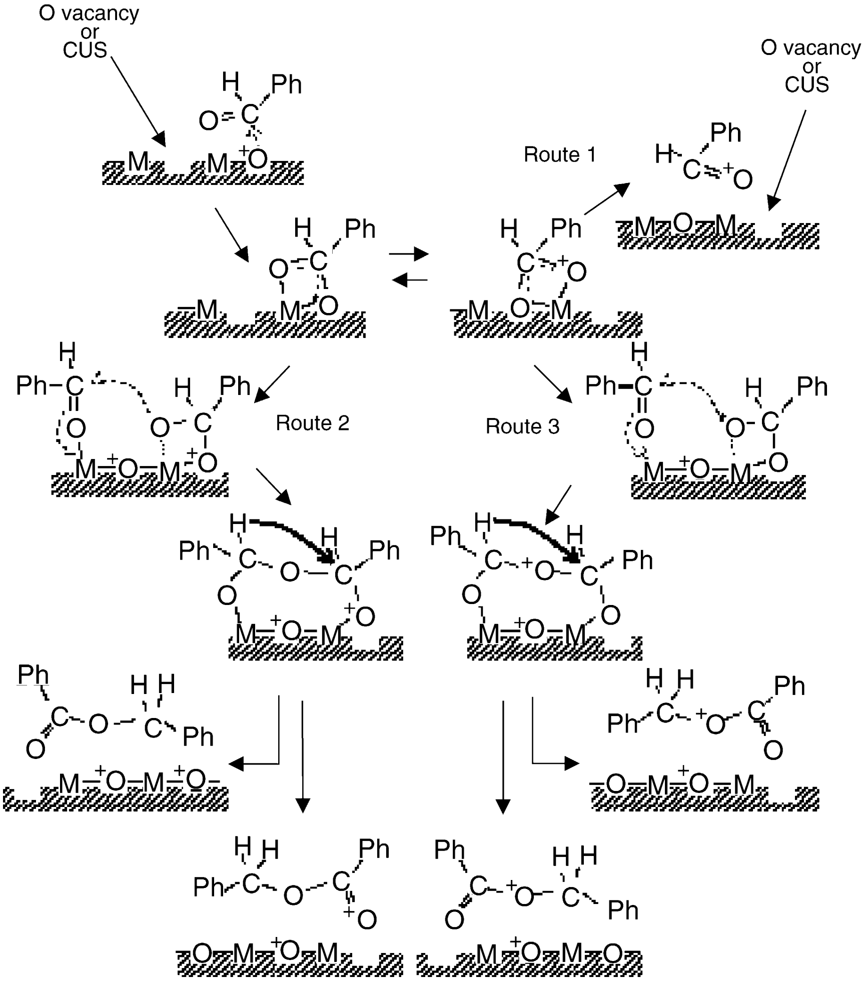


Fig. 5. Mechanisms proposed for Tishchenko reaction of benzaldehyde.

peak at 107/peak at 105 = 0.064, peak at 214/peak at 212 = 0.017

From these values, $M + 2$ enrichment at carbonyl position (107) was calculated to be 0.106–0.064 = 0.042, while $M + 2$ enrichment for whole molecule (214) was calculated to be 0.086–0.017 = 0.069. If ^{18}O were located exclusively in the carbonyl position, $M + 2$ enrichment should have been identical for the carbonyl position and for whole molecule. The experimental results showed that $M + 2$ enrichment is significantly higher for the whole molecule than for the carbonyl position. This demonstrate that ^{18}O is not only in the carbonyl position but also in the bridging position.

The reaction mechanisms proposed for the Tishchenko reaction of benzaldehyde are illustrated in Fig. 5. Benzaldehyde is adsorbed on the M–O pair site at CUS in the form of bidentate. The bidentate aldehyde undergoes O exchange with the surface through route 1 by picking up the surface lattice oxygen and dropping the carbonyl oxygen on the oxygen vacancy. The oxygen of the bidentate aldehyde attacks the electrophilic carbonyl carbon atom of another aldehyde coordinated to the surface metal cation in the monodentate form nearby the bidentate aldehyde. Hydride transfer occurs from the monodentate aldehyde to the bidentate aldehyde to form C–O–C bond resulting in the formation of adsorbed ester in the form of bidentate. On desorption of the ester, the adsorbed ester breaks one of the two C–O bonds through which the adsorbed ester is adsorbed on the surface. One of the C–O breakages results in the incorporation of O originally present as the surface lattice oxygen in the dimerization step. Thus, the oxygen vacancies are continually rearranged during the reaction, and the local topology of the surface is no longer the same as that prior to the reaction. Surface restructuring takes place during the reaction.

It is plausible that the incorporation of the surface lattice oxygen into the product is generally observable in the base-catalyzed reactions of the molecule containing oxygen in such forms as –OH, –O–, –C=O, $-NO_2$, $-SO_2$ etc. In such reactions, active sites are possibly to be dynamic during the reaction.

4. Conclusions

The surface lattice oxygen atoms are incorporated in both the reactant and product in Tishchenko reaction of benzaldehyde over MgO below 343 K. The incorporation of the surface lattice oxygen atoms is involved in both the adsorption–desorption of the reactant and the dimerizatio step. The oxygen exchange between the MgO surface and the reactant and product results in the migration of the active sites of coordinative unsaturated sites over the surface of MgO catalyst during the reaction.

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