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Effects of water vapor in the oxidative dehydrogenation of isobutyric acid to methacrylic acid over iron phosphate catalyst

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The effects of water vapor on the oxidative dehydrogenation of isobutyric acid to methacrylic acid over an iron phosphate catalyst were studied. The presence of water vapor suppresses both the carbon deposit and the formation of phosphorus-rich species on the surface of the catalyst and, as a result, it prevents the degradation in both the catalytic activity and the selectivity which occurs during the reaction, though it has no clear influence on both the redox properties and the structure of the catalyst. The pretreatment of the catalyst with a gas containing water vapor or the reaction in the presence of water vapor restores the activity and selectivity of the degraded catalyst. It is proposed that water plays a role in removing the carbon and oxygenated products from the surface, in suppressing the side reaction, that is, the decomposition of isobutyric acid to propylene and CO, and also in modifying the surface species.

Keywords: iron phosphate; methacrylic acid; isobutyric acid; oxidative dehydrogenation; water effect

1. Introduction

It is known, in patents, that oxidative dehydrogenation of isobutyric acid (IBA) to methacrylic acid (MAA) is promoted selectively with catalysts based on

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phosphates of either molybdenum or iron. Indeed, a good deal of scientific work has been devoted to investigations on this reaction [1–12]. The reaction with molybdenum phosphate catalysts is usually performed at a low temperature of 270–360°C in the presence of an excess of oxygen with respect to IBA and a relatively small amount of water vapor. On the other hand, the reaction with iron phosphate catalysts is usually performed at a higher temperature of 380–430°C with an oxygen/IBA molar ratio of about 0.7 in the presence of a large amount of water vapor. However, the selectivities of IBA to MAA obtained with the two phosphate catalysts seem to be comparable to each other. The most remarkable difference in the catalytic actions between phosphates of molybdenum and iron is the effect of water. As for the reaction with molybdophosphate catalysts, Watzenberger and Emig [6] reported that water hinders the adsorption of IBA but it accelerates the desorption of the products, and that the optimal water/IBA molar ratio is 1 to 2. On the other hand, Dekiouk et al. [9] reported that over an iron phosphate catalyst the rate of MAA formation increases almost linearly with an increase in the partial pressure of water vapor up to about 0.2 atm and it levels off with further increase. It was also found in our recent study [12] that the rate of IBA consumption over an iron phosphate catalyst increases with the partial pressure of water vapor up to 0.2–0.4 atm, much as the results of Dekiouk et al. [9], and that the selectivity to MAA increases steadily with an increase in the partial pressure of water vapor up to about 0.7 atm, while the selectivity to carbon oxides (CO_x) decreases. In this study, we attempted to gain more insight into the effect of water vapor for a more fully understanding of the action of iron phosphate as a catalyst in the oxidative dehydrogenation.

2. Experimental

An iron phosphate catalyst with a P/Fe atomic ratio of 1.2 was prepared according to the procedures described in the preceding study [11]. It was calcined in a stream of air at 500°C for 4 h. The BET surface area was 15 m^2/g.

XRD patterns of powder samples were studied using a Rigaku-Denki, model RAD-RB diffractometer with Cu K_α radiation. The amounts of Fe^{2+} and Fe^{3+} ions in the bulk of catalyst were determined by the redox titration method [13].

XPS measurements were performed as follows. XPS spectra of powder samples were obtained at room temperature with a V.G. Scientific Escalab-200X spectrometer using Mg K_α radiation at 15 kV and 20 mA, and analyzed with a pass energy of 20 eV. The binding energy values (BE) were referred to the C 1s level on the surface as 284.6 eV. The amounts of Fe^{2+} and Fe^{3+} species on the surface were determined by the factor analysis of iron 2p peaks using Fe^{2+} and Fe^{3+} spectra which were obtained from $Fe_2P_2O_7$ and $FePO_4$ standard samples. The P/Fe atomic ratios on the surface were calculated basing on the areas of 2p peaks for phosphorus and iron, the Scofield photoionization cross sections, the mean free paths of the electrons, and the instrumental function which was given by the ESCA manufacturer.

The oxidative dehydrogenation of IBA was conducted with a continuous-flow system at atmospheric pressure as described in the previous studies [4,10–12]. The reaction temperature was 400°C and the feed rates of IBA, oxygen, water, and nitrogen were 21.5, 16.5, 324, and 350 mmol/h, respectively, unless otherwise indicated.

3. Results

3.1. EFFECT OF WATER VAPOR ON THE REACTION

Oxidation of IBA was performed at 400°C over 2.2 g portions of freshly calcined catalyst with feed rates of IBA, oxygen, nitrogen, and water of 21.5, 16.5, 350 and 324 or 0 mmol/h, respectively. The conversion of IBA, yields of MAA, acetone, propylene, and CO_x, and selectivity of IBA and MAA at different times-on-stream are listed in table 1.

In the presence of water vapor, the catalytic activity is relatively stable and the selectivity to MAA increases, to a certain extent, with an increase in the time-on-stream. In the absence of water vapor, the conversion of IBA decreases clearly with the time-on-stream. Moreover, the yields of MAA and acetone become lower, while those of propylene, CO, and CO_2 become higher than those obtained in the presence of water vapor. A marked deposit of carbon on the catalyst was observed in the absence of water vapor.

On the other hand, IBA was passed over 2.2 g portions of catalyst in the absence of oxygen at 400°C with feed rates of IBA, nitrogen, and water of 21.5, 350, and 324 or 0 mmol/h, respectively. The results are shown also in table 1.

In the presence of water vapor but absence of oxygen, the conversion of IBA and the yields of MAA, acetone, and CO_2 are low and they decrease markedly with an increase in the time-on-stream. As a result, propylene and CO become the main products. No carbon deposit was observed. In the absence of both oxygen and water, however, the conversion of IBA becomes much higher than that obtained in the presence of water. The main products are propylene and CO. As in the case where water is present, the yields of MAA, acetone, and CO_2 are low and they decrease with time. A marked deposit of carbon was observed.

3.2. EFFECT OF WATER VAPOR ON THE SURFACE PROPERTIES OF THE CATALYST

Oxidation of IBA was performed over 2.2 g portions of freshly calcined catalyst samples in the presence and absence of water vapor. The values of P/Fe and $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratios on the surface measured by XPS for the catalyst sam-

Table 1
Effects of water and oxygen on the reaction of isobutyric acid [a]

Feed rate (mmol/h)				Contact time (s)	Reaction time (h)	IBA conv. (%)	S to MAA (mol%)	Yield (mol%)				
IBA	N_2	O_2	H_2O					MAA	acetone	C_3H_6	CO_2	CO
21.5	350	16.5	324	0.4	0.8	80.0	76.5	61.1	10.6	1.6	3.2	3.9
					2.2	92.6	77.4	71.6	11.3	0.6	5.6	3.7
					3.8	87.6	78.0	68.5	9.7	0.4	6.5	3.1
21.5	350	16.5	0	0.73	0.8	72.8	50.0	36.4	6.2	10.5	10.4	8.3
					2.2	50.6	46.8	23.7	3.3	9.0	9.1	5.5
					3.7	43.5	47.4	20.7	2.7	7.5	9.4	5.2
21.5	350	0	324	0.41	0.8	20.0	33.9	6.8	1.1	8.0	0.0	4.5
					2.3	16.2	12.3	2.0	0.4	9.0	0.0	4.8
					3.5	15.0	5.3	0.8	0.2	9.0	0.0	5.0
21.5	350	0	0	0.77	0.7	67.6	8.1	5.5	0.9	33.0	0.0	28.2
					2.0	70.5	2.4	1.7	0.4	45.0	0.0	24.4
					3.2	59.3	1.3	0.8	0.2	37.0	0.0	21.3

[a] IBA = isobutyric acid; MAA = methacrylic acid; C_3H_6 = propylene; conv. = conversion of IBA; S = selectivity of IBA.

ples used in the reaction are listed together with the values of $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios in the bulk measured by redox titration (table 2).

During the oxidation reaction in the presence of water vapor, the fresh catalyst is gradually reduced, though the rate is slow. However, the extent of reduction during the reaction in the absence of water vapor, is much lower. It should also be noted that the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios on the surface measured by XPS are in agreement with those in the bulk measured by chemical analysis, regardless of the presence or absence of water vapor.

The P/Fe ratio on the surface of the catalyst used in the presence of water vapor remains 1.2, independent of an increase in the time-on-stream. This value is the same as that in the bulk. On the other hand, the P/Fe ratio on the catalyst used in the absence of water is 1.5. This means that the content of phosphorus on the surface of the catalyst used in the absence of water vapor is higher than that in the bulk.

3.3. EFFECT OF WATER VAPOR ON THE REDUCTION OF THE CATALYST

IBA was passed over 1.5 g portions of catalyst samples at 400°C in the absence of oxygen and either in the presence or absence of water. The feed rates of IBA, nitrogen, and water were 21.5, 350, and 324 or 0, respectively. The extents of reduction of iron ions in the bulk, that is, the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios, are shown as a function of the time-on-stream in fig. 1.

The freshly calcined catalyst samples consist only of Fe^{3+} ions. The extent of reduction increases steadily with an increase in the time-on-stream and it is scarcely influenced by the presence or absence of water in the feed. It should be noted that a marked deposit of carbon on the catalysts was observed in the absence of water, while no carbon deposit was observed in the presence of water.

Table 2
Surface properties of the catalyst samples used in the oxidation of IBA

Sample no.	Reaction time (h)	$Fe^{2+}/(Fe^{2+}+Fe^{3+})$		P/Fe	
		chemical	ESCA	nominal	ESCA
in the presence of water vapor					
1	0	0.00	0.00	1.2	1.16
2	1	0.03	0.07	1.2	1.31
3	2	0.07	0.12	1.2	1.23
4	4	0.12	0.18	1.2	1.21
5	8	0.18	0.19	1.2	1.24
6	16	0.29	0.27	1.2	1.27
in the absence of water vapor					
7	5	0.07	0.11	1.2	1.45
8	8	0.05	0.08	1.2	1.45
9	16	0.05	0.06	1.2	1.53

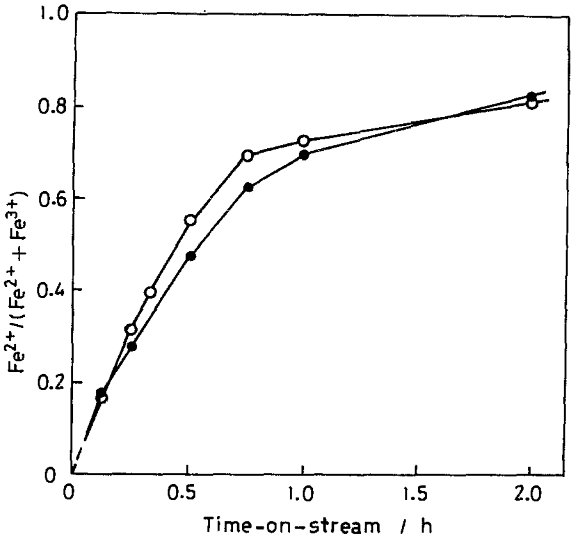

Fig. 1. Reduction of iron phosphate catalyst with IBA at 400°C. (○) In the presence of water vapor, (●) in the absence of water vapor.

The freshly calcined catalyst samples contain both the $FePO_4$ phase and an unknown phase. The unknown phase is characterized with XRD peaks at $2\theta = 20.00°, 20.95°, 22.50°$ and is considered to be an intermediate phase formed during the phase change from the amorphous phase to the $FePO_4$ phase due to a rise in the calcination temperature [10]. The unknown phase is designated hereafter as X-phase.

As the extent of reduction increases, the $FePO_4$-phase, X-phase, and amorphous phase are transformed to the $Fe_2P_2O_7$ phase [14] via another unidentified intermediate phase characterized with XRD peaks at $2\theta = 19.98°, 21.24°, 24.70°, 35.04°, 35.54°, 50.68°$, and $63.12°$ and having a $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio of about 0.5 [11]. This intermediate phase is designated hereafter as B-phase. It was also found that the influence of water vapor on the structure of catalyst samples is not observed.

3.4. EFFECT OF WATER VAPOR ON THE REOXIDATION OF THE REDUCED CATALYST

The catalyst samples were reduced in a stream of hydrogen at 480°C for 12 h. The obtained catalyst samples consisted of $Fe_2P_2O_7$ phase with a good crystallinity (the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio was 0.88). Then, air or a mixture of air and water vapor was passed at 400°C over 1.5 g portions of the reduced catalyst samples. With an increase in the time-on-stream, the catalyst samples were reoxidized steadily, that is, the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio decreased (fig. 2). It was also found that the extent of reoxidation is scarcely influenced by the presence of water vapor.

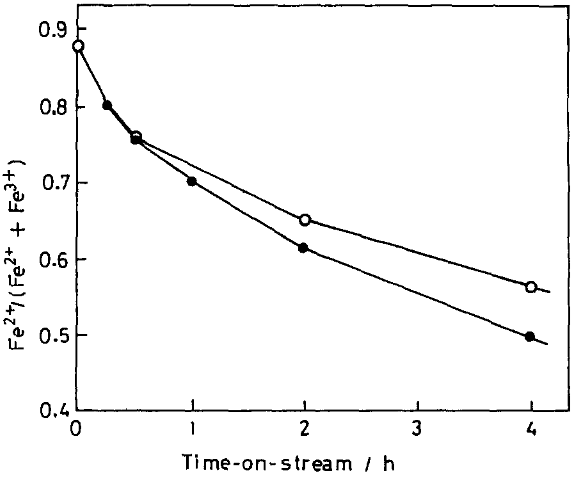

Fig. 2. Reoxidation of reduced iron phosphate catalyst with air at 400°C. (○) In the presence of water vapor, (●) in the absence of water vapor.

As increasing the extent of reoxidation, the $Fe_2P_2O_7$ phase was transformed to a new phase whose XRD patterns are similar to those of $Zn_2P_2O_7$: a clear peak at $2\theta = 29.50°$. This new phase is designated hereafter as Y-phase. It was concluded that influence of water vapor on the variation in the structure is not observed.

3.5. EFFECT OF THE PRETREATMENT OF THE FRESH CATALYST ON THE REACTION

About 4 g portions of freshly calcined catalyst samples were treated with different gas mixtures for 4 h. The effects on the catalytic performance, structure, and valence states of iron ions in the bulk were studied (table 3).

The results are summarized as follows.

(1) The freshly calcined catalyst consists of only Fe^{3+} ions and contains $FePO_4$ as the main phase with a small amount of X-phase. The extent of reduction of Fe^{3+} ions, that is, the $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ ratio, increases slowly as the time-on-stream increases. First, the X-phase disappears and the B-phase appears, and then the $FePO_4$ phase is transformed to the B-phase.

(2) By a pretreatment with a gas consisting of nitrogen and water vapor at 480°C for 4 h, both the conversions of IBA and selectivity to MAA become lower at the beginning of the reaction, but after about 3.5 h on stream, they are restored to the same levels as those obtained from the untreated catalysts.

(3) A pretreatment with the reaction feed gas-mixture without water vapor induces a marked decrease in both the activity and selectivity to MAA and a marked deposit of carbon on the catalyst. However, it does not induce any clear change in both the structure and valence state of iron ions. The degraded catalyst performance is restored gradually with the reaction performed in the presence of water vapor.

Table 3
Effects of pretreatments for fresh iron phosphate catalyst on the reaction [a]

Test no.	Feed rates (mmol/h) of pretreatment gas				Reaction time (h)	IBA conv. (%)	Select. to MAA (mol%)	$Fe^{2+}/(Fe^{2+}+Fe^{3+})$	Phases observed in XRD spectra	
	IBA	N_2	O_2	H_2O					main	minor
(1)	none				0			0.0	$FePO_4$	X-phase
					0.8	80.0	76.5			
					2.2	92.6	77.0			
					3.8	87.6	78.5			
					4.3	86.2	78.5	0.12	$FePO_4$	B-phase
					7.1	87.3	80.0	0.18		
					18.0			0.28	$FePO_4$	B-phase
(2)	0	350	0	324	0			0.0	$FePO_4$	
	(480°C)				0.8	52.4	72.1			
					2.2	72.7	76.8			
					3.5	86.0	78.0			
					4.0			0.15	$FePO_4$	B-phase
(3)	21.5	350	16.5	0	0			0.06	$FePO_4$	X-phase
	(400°C)				0.8	49.1	70.5			
					2.2	69.0	76.5			
					3.5	77.8	78.2			
					4.0			0.15	$FePO_4$	B-phase
(4)	21.5	350	16.5	0	0			0.06	$FePO_4$	X-phase
	(400°C)				0.8	63.3	73.5			
	followed by				0.22	76.2	75.1			
	0	350	0	324	3.5	78.5	80.0			
	(400°C)				4.0			0.15	$FePO_4$	B-phase
(5)	21.5	350	0	324	0			0.86	$Fe_2P_2O_7$	–
	(400°C)				0.8	85.1	80.1			
					2.0	88.6	81.3			
					3.6	89.0	82.0			
					4.1			0.82	$Fe_2P_2O_7$	Y-phase
(6)	21.5	350	0	0	0			0.84	$Fe_2P_2O_7$	Y-phase
	(400°C)				0.8	39.0	67.5			
					2.2	65.0	74.1			
					3.8	76.1	76.0			
					4.3			0.69	Y-phase	$Fe_2P_2O_7$
(7)	21.5	350	0	0	0			0.91	$Fe_2P_2O_7$	Y-phase
	(400°C)				0.8	62.7	75.0			
	followed by				2.2	73.4	77.6			
	0	350	0	324	3.6	78.1	80.0			
	(400°C)				4.1			0.88	$Fe_2P_2O_7$	Y-phase

[a] Pretreatment time = 4 h. Reaction conditions: temperature = 400°C; contact time = 0.4 s. Catalyst: freshly calcined catalyst.

(4) From a pretreatment with the reaction feed gas-mixture without water vapor followed by another pretreatment with a mixture of nitrogen and water vapor, it is found that the pretreatment with water vapor induces a restoration in both the activity and selectivity.

(5) A pretreatment with the reaction feed gas-mixture without oxygen induces marked changes in the structure and valence states of iron ions and, moreover, it induces clear increases in both the activity and selectivity. Formation of a small amount of Y-phase was observed in the catalysts after 4 h of use in the reaction.

(6) A pretreatment with the reaction feed mixture containing neither oxygen nor water induces a marked deposit of carbon and, moreover, it induces decreases in both activity and selectivity and changes in the structure and valence states of iron ions. However, the activity and selectivity are restored, to a creation extent, as an increase in the time of reaction performed in the presence of water.

(7) The results obtained from a pretreatment with the reaction feed mixture containing neither water nor oxygen followed by another pretreatment with a mixture of water vapor and nitrogen, indicate that the pretreatment with water vapor plays a role in restoring the activity and selectivity.

3.6. EFFECT OF THE PRETREATMENTS OF THE REDUCED CATALYST ON THE REACTION

On the other hand, 4 g portions of the catalyst samples that had previously been reduced in a stream of hydrogen at 480°C for 24 h, were treated with different gas mixtures (table 4).

The results are summarized as follows.

(1) The catalyst reduced with hydrogen shows almost the same structure, valence states of iron ions, and catalytic performances as those obtained with the catalysts reduced by IBA.

(2) By an air treatment performed at 480°C for 8 h in the absence of water, the reduced catalyst sample was reoxidized, that is, the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratio decreased from 0.96 to 0.28, and the color changed from slightly grayish white to red-brown. In the XRD spectra, the peaks corresponding to $Fe_2P_2O_7$ disappear and those to the Y-phase appear. The catalytic activity decreases slightly with the pretreatment. The reoxidized catalyst is rapidly re-reduced from 0.28 to 0.77 with only 3 h of use in the reaction.

(3) By an air treatment performed in the presence of water vapor, the catalyst samples are reoxidized, to the same extent as those oxidized in the absence of water vapor. However, it should be noted that a small amount of $FePO_4$-phase was observed besides the Y-phase in the XRD spectra. The color of the samples reoxidized in the presence of water vapor is brownish gray. The catalytic activity was a little higher than that obtained with the samples reoxidized in the absence of water vapor.

(4) An air-treatment in the absence of water followed by another treatment

Table 4
Effects of pretreatment for reduced iron phosphate catalysts on the reaction

Test no.	Pretreatment	Reaction time (h)	IBA conv. (%)	Select. to MAA (mol%)	Fe^{2+}/ (Fe^{2+} + Fe^{3+})	Phases by XRD spectra	
						main	minor
(1)	none	0			0.96	$Fe_2P_2O_7$	–
		0.8	79.0	82.0			
		2.5	80.7	82.5			
		3.0			0.86	$Fe_2P_2O_7$	Y-phase
(2)	reoxidation by air, 480°C, 8 h (in the absence of water)	0			0.28	Y-phase	–
		0.8	74.7	81.5			
		2.5	76.7	81.5			
		3.0			0.77	Y-phase	$Fe_2P_2O_7$
(3)	reoxidation by air, 480°C, 8 h (in the presence of water)	0			0.38	Y-phase	$FePO_4$
		2.5	83.7	82.5			
		3.0			0.66	Y-phase	$Fe_2P_2O_7$
(4)	reoxidation by air, 480°C, 8 h followed by treatment with water + N_2, 480°C, 8 h	0			0.27	Y-phase	$FePO_4$
		2.5	85.0	81.0			
		3.0			0.60	Y-phase	$Fe_2P_2O_7$
(5)	reoxidation by air, 480°C, 8 h followed by treatment with IBA + water + N_2, 400°C, 4 h	0			0.90	$Fe_2P_2O_7$	–
		2.5	85.0	80.5			
		3.0			0.84	$Fe_2P_2O_7$	Y-phase

with a mixture of water vapor and nitrogen induces no clear change in both the structure and valence states of iron ions, but it induces an increase in the activity and a change in color from brown to brownish gray.

(5) By an air-treatment in the absence of water followed by another treatment with the reaction feed mixture without oxygen, the catalyst samples are re-reduced to $Fe_2P_2O_7$ and the catalytic activity is restored.

4. Discussion

The catalytic performance of a metal oxide in selective oxidation is believed to be governed by two kinds of functions: (1) reduction–reoxidation (redox) and (2) activation of reactant molecules and release of products [15].

The results of the XPS study shown in table 2 indicate that the P/Fe ratio on the surface of catalysts used for the oxidation in the presence of water vapor is the same as that in the bulk, while the P/Fe ratio on the surface of catalysts used in the absence of water vapor is higher than that in the bulk. This suggests that water vapor prevents the formation of phosphorus-rich surface layers that seem to be less active as active sites for the oxidation [10].

The reduction of iron phosphate performed with IBA in the absence of water vapor induces a marked deposit of carbon, while the reduction performed in the presence of water vapor induces no deposit of carbon. Even in the presence of oxygen, a marked amount of carbon is deposited on the surface during the oxidation of IBA performed in the absence of water, and both the catalytic activity and selectivity to MAA decrease gradually as the time-on-stream increases. These findings suggest that the catalytic activity is hindered by the deposit of carbon or other oxygenated products, and that the water vapor plays a role in removing the carbon and oxygenated products from the surface.

Further, as may be seen from tables 3 and 4, the catalytic performances, which are degraded by the reaction or the treatments performed in the absence of water, are restored gradually when increasing the time of the reaction or that of the treatment performed in the presence of water. Therefore, it is considered that the regeneration of degraded catalysts can be ascribed to the removing of deposit of carbon on other oxygenated products from the surface by water vapor.

The decrease in the selectivity to MAA induced by the reaction performed in the absence of water is considered to be caused by the increase in the activity for the formation of propylene and CO (table 1).

On the other hand, in the absence of oxygen, the yields of the oxidation products such as MAA and acetone become much lower than those obtained in the presence of oxygen and, further, they decrease with an increase in the time-on-stream. This can be reasonably understood from a lack in the oxygen source. However, it should be noted that the yields of propylene and CO are enhanced in the absence of oxygen.

The formation of propylene and CO is greatly promoted by the absence of both water and oxygen. It is therefore likely that the decomposition of IBA to propylene and CO,

$$CH_3{-}CH(CH_3){-}COOH \rightarrow CH_3CH{=}CH_2 + CO + H_2O\,,$$

which is reported to be promoted by acidic sites [16] and which takes place in parallel with the oxidative dehydrogenation to MAA, is suppressed by cooperative action of water and oxygen.

Interestingly, it was recently found that the influence of water vapor on the catalytic activity and selectivity is small in the oxidative dehydrogenation of isobutyronitrile to methacrylonitrile that is performed at a higher temperature of 480°C [17]. It is considered that the oxygenated products are removed relatively easily from the surface without the aid of water vapor because the interaction between the products and catalyst surface is small at the high temperature. This finding may also support the view that water vapor plays a role in removing the products from the surface.

It was found in this study that the presence of water vapor does not modify the variation of structure during the reduction–reoxidation processes. However, the presence of water vapor in the gas used for the pretreatments has a large influence on the catalytic performances, even when no deposit of carbon is observed (tables 3 and 4). For example, the catalyst obtained by reoxidation of reduced catalyst in the absence of water vapor shows a clearly lower activity than that obtained by reoxidation in the presence of water vapor, though both catalysts show a similar XRD pattern (Y-phase). Much as the results of the preceding study [11], it is hard to find any clear correlation between the catalytic performances and the structure or valence states of iron ions in the bulk. As mentioned above, water vapor seems also to play a role in modifying the surface species, though it is still hard to clarify the surface active species.

In conclusion, it is at least clear that water vapor plays a role in promoting the removing of reaction products from the surface and, as a result, in stabilizing and regenerating the active sites, moreover, in suppressing the catalytic activity for the decomposition of IBA to propylene and CO. It is also likely that water vapor plays a role in preventing the formation of phosphorus-rich surface species that are less active as active sites. However, water vapor has no influence on the redox property in the bulk and on the structure in the bulk.

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