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Oxidative Dehydrogenation of 1-Butene over Manganese Oxide Octahedral Molecular Sieves

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Steady state kinetic studies of the oxidative dehydrogenation of 1-butene to 1,3-butadiene have been carried out on manganese oxide octahedral molecular sieve (OMS) and octahedral layered (OL) materials. Process parameters such as temperature, feed composition of 1-butene and oxygen, and feed flow rates were varied to study their effect on the activity and selectivity toward the oxidative dehydrogenation process. In addition to process parameters, modifications in the catalyst such as the ion-exchange of tunnel cations and framework substitution of manganese cations were also implemented in order to observe their effects on catalytic activity and the selectivity of 1,3-butadiene production. The ion-exchanged OMS and OL materials showed rapid deactivation with time when subjected to reaction mixtures of 1% 1-butene/0.7% oxygen/Ar and 1% 1-butene/1.1% oxygen/Ar at reaction temperatures greater than 400°C. Their selectivity toward 1,3-butadiene were typically from 15–20% (yield of 4–6%). The other products were *cis* and *trans* 2-butene and carbon dioxide and water (40–60% selectivity). Much of the oxidation was therefore nonselective. XRD data have shown that there is a phase change of the original precursor to a mixture of Mn_3O_4/MnO or plain MnO, in some cases after exposing the catalyst to reaction conditions for about 1–2 h. Framework substitution of some of the manganese with copper (OMS and OL), however, has led to higher yields and selectivities toward 1,3-butadiene. [Cu] OL-1 showed a yield of 11.8% and a maximum selectivity of 26% toward 1,3-butadiene. [Cu] OMS-1 shows a dramatically high selectivity of 36% and a yield of 11% toward 1,3-butadiene. The effect of framework substitution seems to also impede the phase change to Mn_3O_4 (Hausmannite). The TPR spectra also show an increase in the lattice oxygen peak by about 40°C, in comparison with ion-exchanged OMS. This is sufficient indication that framework substitution of manganese by copper, partially, has enhanced the stability of the catalyst and improved its capacity for selective oxidation.

INTRODUCTION

Octahedral molecular sieves (OMS) may be described as tunnel structures formed by the edge sharing of MnO_6 octahedral units (1–3). Tunnel structures of interest in our research group are of two types—3 × 3 (6.9 Å pore opening, OMS-1) and 2 × 2 (4.6 Å pore opening, OMS-2), where each edge-shared unit is MnO_6 (1–3). In its natural mineral form, the OMS-2 is available as cryptomelane (potassium cation in the tunnel, KMn_8O_{16}) and as hollandite (barium cation in the tunnel, $BaMn_8O_{16}$). Other natural mineral forms of OMS-2 are manjiroite ($NaMn_8O_{16}$) and coronadite ($PbMn_8O_{16}$) (4).

Todorokites are naturally occurring manganese oxides, which contain, predominantly, a 3 × 3 tunnel structure formed by triple chains of MnO_6 edge sharing octahedra. According to Turner *et al.* (5), todorokites are available in deep sea manganese nodules containing high concentrations of copper and nickel. Therefore, it is probable that such metals substitute for Mn^{2+} in the octahedral framework. Naturally occurring todorokites are also poorly crystalline, impure in composition, and co-exist with several manganese oxide minerals. It is not possible to study their catalytic properties without isolating the individual phases. The 3 × 3 structured phase (OMS-1) occurring in natural todorokites has attracted considerable interest owing to the large size of the tunnel (6.9 Å) and its cation exchange behavior, which are very similar to zeolites (3). Other than the 3 × 3 structures, naturally occurring todorokites contain 3 × 2, 3 × 4, 3 × 5 tunnel structured phases, in the form of a random intergrowth. The synthesis of 3 × 3 tunnel structured materials has been described in a patent (4).

Natural manganese nodules have been used in the catalytic oxidation of carbon monoxide, methane, and butane (6); reduction of nitric oxide with ammonia (7), and the demetallation of topped crude in the presence of hydrogen (8). The difference between these natural manganese nodules and the synthetic molecular sieve materials used is that the latter is very homogenous in its structure making it very easy to correlate reactivity with structure and phase changes. The substitution of framework cations and ion exchange of extra-framework cations may be carried out in OMS-1 and OMS-2 systems and have been mentioned in a patent application (4). Some of the preliminary work in characterization and examination of thermal stability of the OMS materials has been done in our group by Yin *et al.* (1, 2).

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Yin and co-workers (1) have been able to characterize synthetic todorokite type materials by temperature programmed desorption (TPD), reduction (TPR), and pulse reduction of the catalyst by carbon monoxide. The catalysts investigated are ion-exchanged forms of OMS-1 (1). The ions used for the exchange process include: Cu^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, and Co^{2+}. Typically, for most of these cases, the TPR (5% CO/He) data reveal multiple oxygen peaks, all of them appearing before 450°C (1), although the structure starts to disintegrate by 300°C.

Similar TPR, TPD, and X-ray diffraction (XRD) data have been presented by Yin *et al.* (2) for OMS-2 catalysts, ion-exchanged with Cu^{2+}, Ni^{2+}, Co^{2+}, and K^+. Yin and co-workers have tried to study the role of the cation in influencing the thermal stability of the catalysts. They have also attempted to regenerate the reduced catalyst by pulse oxidation with 85% regenerability. The structure of the OMS-2 begins to collapse irreversibly at about 300°C, when exposed to a 5% CO/He mixture (2). Although the oxygen is incorporated back into the material, the structural transformation is irreversible (2). Yet it is not very clear how the process conditions affect the deactivation under steady state reactions and what kind of phase transformations occur over an extended period of time on stream. The objective of this paper is to address some of these questions.

One of the reactions of interest is the selective oxidation or oxidative dehydrogenation of 1-butene. The oxidative dehydrogenation of 1-butene leads to the formation of 1,3-butadiene, and the commercial catalyst used for this purpose is zinc ferrite (9). Other catalysts of research interest include bismuth molybdovanadate (with iron) (10) and magnesium orthovanadates (11). The selectivity toward 1,3-butadiene is very large (>80%) in most of these cases. On a commercial level, zinc ferrites (with chromium, magnesium, and manganese in variable amounts) show about 65% conversion per pass with 93% selectivity toward 1,3-butadiene (9). Under process conditions, the feed mixture includes butenes, air, and steam in optimal ratios. Temperatures of the bed reach a maximum of not more than 575°C (9).

In this paper, the partial oxidation of 1-butene has been studied, using various ion-exchanged forms of OMS-1, OL-1, and OMS-2, and also cations substituted in the framework of OL-1 and OMS-1. The thermal stability of the catalysts, the resultant phase changes, and deactivation during steady state reactions have been investigated, in addition to optimization of process conditions for the reaction. Another objective of this study is to use oxidative dehydrogenation as a probe reaction to examine the active sites, the phase changes, and the deactivation mechanism in the catalyst of interest. An evaluation of such factors is essential in order to synthesize improved materials with more desirable catalytic properties.

EXPERIMENTAL PROCEDURES

The starting materials used in this work have been OMS-1, OMS-2, and OL-1. The nature and general synthetic procedures for these materials have been discussed in the previous section. The primary techniques used in observing the behavior of these catalysts have been steady state catalytic oxidation reactions (analysis by GC/FID), temperature programmed reduction, and X-ray powder diffraction.

Synthesis, Ion-Exchange, and Framework Substitution

The methods of synthesizing OMS-1 and OMS-2 have a common step of reacting the manganese cation and the permanganate anion in an aqueous reaction medium. Upon carrying out the reaction under acidic conditions and subsequent autoclaving at temperatures ranging from 80 to 140°C in the presence of counter cation with ionic diameters of 2.3 to 4.6 Å, the OMS-2 structure is formed. If the reaction is carried out under strongly basic conditions, a layered manganese oxide precursor (OL-1) has been observed to form. The OL-1 is ion exchanged and calcined at high temperatures to form OMS-2 (12).

Steady State Kinetics Experiments

For the studies of oxidative dehydrogenation of 1-butene, different ion-exchaged OMS-2 materials (Cu^{2+}, Fe^{3+}, Cr^{3+}, K^+), OMS-1 (Cu^{2+}, Fe^{3+}), amorphous MnO_x, and framework substituted forms of OMS-1 and OL-1 have all been used. The preparations of the catalysts have been carried out using the recipes discussed in the previous section and in the references (1–3, 12). Details of framework substitution of copper in OMS-1, OL-1, and OMS-2 will appear soon (17).

The reaction was carried out in a stainless steel microreactor and the exit stream from the reactor was connected to the sampling loop of a gas chromatograph. The gas chromatograph was a CARLE 311 with a flame ionization detector (FID) and was interfaced to an HP integrator.

The feed gases used in this reaction are mixtures of 1-butene and oxygen in various ratios. The typical process parameters which have been varied for this experiment are the temperature of the reaction, the flow rate of the feed gas, the weight of the catalyst, and the 1-butene/oxygen ratio.

Our gas mixtures were composed of 1% 1-butene with 0.7, 1.1, 2, and 3% oxygen. The effect of the feed ratio, the temperature, and the space velocities of the feed on the overall conversion, yield, and selectivity toward 1,3-butadiene have been studied in this set of experiments.

In both cases, only hydrocarbons have been detected and measured due to the use of an FID detector. The column used for separation of the hydrocarbons was ALLTECH Gas Chrom, CS 100/120 mesh, which gave excellent sensitivity and resolution upon optimizing the hydrogen and helium flow rates. Operation of the column at room temperature was found to be adequate in separating the hydrocarbons.

Since the detector is an FID, the oxygen in the feed could not be measured, nor could the carbon dioxide coming off as a product. The hydrocarbon feed and the hydrocarbon products were measured, whereas the carbon dioxide was evaluated by a material balance. To check for any other oxygenated products, a mass spectrometric analysis with a GC-MS was carried out. No other oxygenates were identified except carbon dioxide and water. Therefore, the estimation of CO_2 from the material balance was justified.

Studies of Stability and Phase Changes

The best way to monitor stability is by TPR followed by XRD. XRD may also be carried out after steady state reaction over a period of time.

TPR experiments with a 5% CO–He mixture were conducted in the setup as described below. A quartz reactor with a diameter of about 1/2 in. was loaded with a small bed of catalyst (about 20 mg) and subjected to a CO–He flow of 35–40 cc/min. The effluent from the reactor passed through a liquid nitrogen trap, which trapped water and CO_2 evolved from the TPR. The effluent was stripped of the water and CO_2 and passed through a thermal conductivity detector (TCD) located further downstream. The signal from the TCD was a measure of only the unreacted CO in the effluent. The measurement of the residual CO signal was indicative of the amount of oxygen consumed during the course of the reduction process. The heating rate used here was approximately 20°C/min. Usually, the reactor was heated from room temperature to about 600°C.

XRD data may be obtained either after a steady state reaction over a period of time or after a TPR experiment, by which time all phase transformations would have occurred. The XRD powder patterns were collected using a SCINTAG 2000 XDS diffractometer with Cu $K\alpha$ X-ray radiation. A beam voltage of 45 kV and a beam current of 40 mA were maintained for all the patterns. Typically the scan speed used was about 2°/min. For the OMS materials, variation of 2θ from 5° to 60° was optimal.

RESULTS

Oxidative Dehydrogenation of 1-Butene–Steady State Experiments Cu–OMS-2: Feed–1% 1-Butene/Argon

The oxygen species from the catalyst are utilized for the oxidation as there is no feed oxygen. The selectivity of the 1,3-butadiene dropped, as did the conversion. After this initial drop, isomerization of 1-butene to 2-butenes (*cis* and *trans*) continued to occur, which caused the overall conversion to rise after about 40 min or so (Fig. 1). After an hour, isomerization appears to be the only reaction occurring.

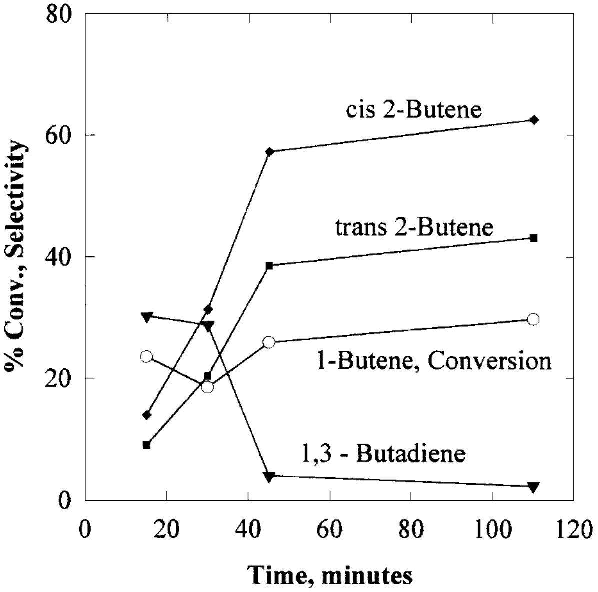

FIG. 1. Steady state kinetics with 1% 1-butene/Ar feed. $T = 450°C$, Catalyst: Cu–OMS-2. $W = 39.9$ mg, $Q = 27$ cc/min.

Cu–OMS-2: 1% 1-Butene/0.7% O_2/Argon

Feed oxygen is vital to the process of replenishing the used oxygen from the catalyst. Since the reaction of interest was the oxidative dehydrogenation of 1-butene, the oxygen used in the feed was slightly more than the stoichiometric requirement for reaction but much smaller than the stoichiometric requirement for total oxidation of the hydrocarbon. The feed oxygen was thus kept at 0.7% along with 1% 1-butene. The results are shown in Fig. 2 and summarized

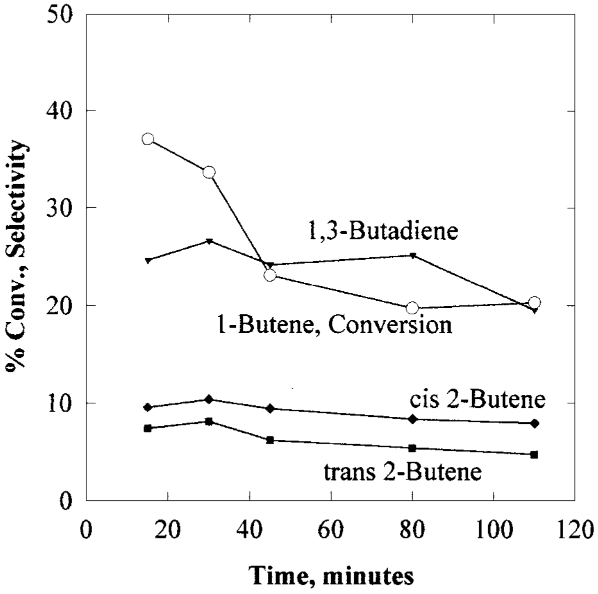

FIG. 2. Steady state kinetics with 1% 1-butene/0.7% O_2/Ar feed. $T = 450°C$, Catalyst: Cu–OMS-2. $W = 39.9$ mg, $Q = 27$ cc/min.

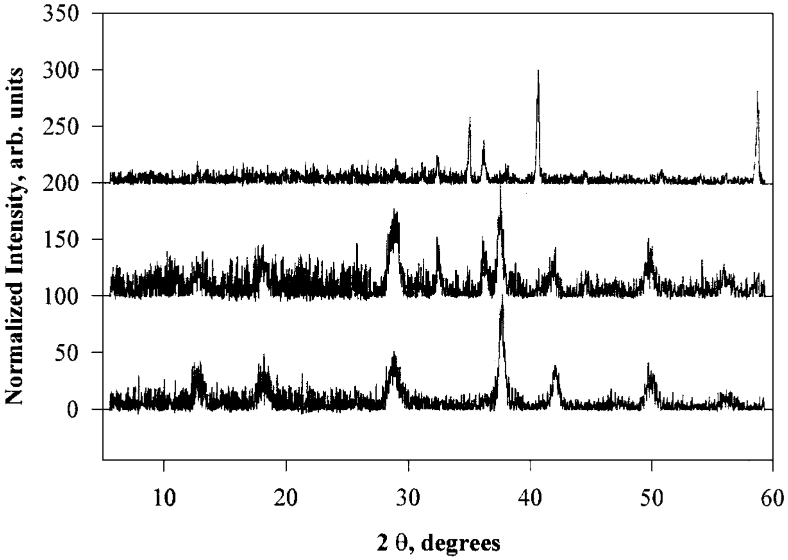

FIG. 3. X-ray powder diffraction–ion-exchanged Cu–OMS-2: Change of structure with reaction.

in Table 1. The production of 1,3-butadiene has been stabilized at higher times, despite the initial deactivation resulting in phase change. The final phase of the catalyst is a mixture of Mn_3O_4 (Hausmannite) and MnO, as shown in the XRD data (Fig. 3).

Comparison of Several Types of Ion-Exchanged Catalysts

Steady state kinetics data for fresh Cu–OL-1 are shown in Fig. 4. These data are for Cu^{2+} ions exchanged into the layered OL-1 material. The 1-butene conversion decreases significantly with time on stream. The *cis*-2 butene yield is higher than either *trans*-2 butene or 1,3 butadiene products. Cu^{2+} ion-exchanged into the original K–OMS-2 and other ion-exchanged forms of OMS-2 were tried as oxidation catalysts such as Cr^{3+} exchanged OMS-2, Fe^{3+} exchanged OMS-2, and the original K–OMS-2. The final forms of the catalysts after the reaction are predominantly MnO. Results obtained from steady state experiments for various OMS-2 catalysts are shown in Table 2.

TABLE 1

Steady State Reaction Data—1% 1-Butene with 0.7% Oxygen in Feed

T (°C)	Initial conv. (X_i)	Final conv. (X_f)	Sel. (1,3-B)	Sel. (2-B)	Sel. (CO_2)
450	37%	19.7%	19.0%	14.5%	66.5%
475	47%	22.2%	19.0%	20.6%	60.4%
505	36%	27.7%	17.2%	36.2%	46.6%
525	31.7%	25.2%	15.6%	47.9%	36.5%

Note. Products = 1,3-butadiene, *cis* and *trans* 2-butene, CO_2, and water. Catalyst = Cu–OMS-2; Feed flow rate = 26–28 cc/min; Weight of bed = 40–42 mg. Selectivities are after 1–1.5 h of reaction, final values.

Fe–OMS-2 system shows the highest yield (6.8%) and selectivity (22.1%) towards 1,3-butadiene (Table 2). Deactivation in Fe–OMS-2 leads to a final value of 5.5% for the yield of 1,3-butadiene. The isomerization reaction leading to the formation of 2-butenes is minimal at lower temperatures but is an important reaction at temperatures of 500°C. In most of these systems, the selectivity toward formation of CO_2 and water ranges from 45 to 55%.

The results for some assorted systems such as Fe–OMS-1, amorphous manganese oxide (MnO_x), pure commercial

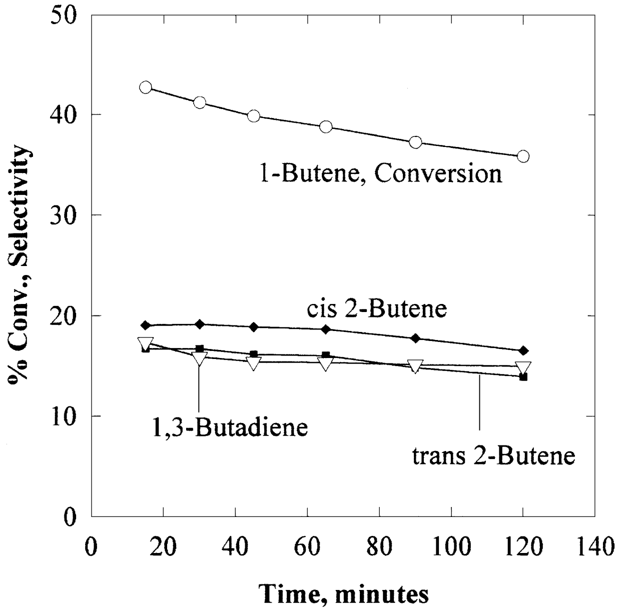

FIG. 4. Steady state kinetics with 1% 1-butene/1.1% O_2/Ar feed. T = 500°C. W = 22.5 mg. Q = 40 cc/min. Catalyst: Fresh Cu–OL-1.

TABLE 2

Comparison of Some Ion-Exchanged Forms of OMS-2

	System			
Y, S, X	Cu–OMS-2	K–OMS-2	Cr–OMS-2	Fe–OMS-2
X_i (%)	24.3%	24.9%	30.8%	30.6%
X_f (%)	20.9%	19.3%	24.2%	24.9%
$S_{1,3\text{-B},i}$ (%)	19.3%	19.4%	17.4%	22.1%
$S_{1,3\text{-B},f}$ (%)	16.7%	15.2%	14.0%	22.2%
$S_{2\text{-B},i}$ (%)	33.0%	28.8%	35.5%	32.8%
$S_{2\text{-B},f}$ (%)	28.0%	19.6%	34.3%	27.7%
$Y_{1,3\text{-B},i}$ (%)	4.7%	4.8%	5.4%	6.8%
$Y_{1,3\text{-B},f}$ (%)	3.5%	2.9%	3.4%	5.5%
$Y_{2\text{-B},i}$ (%)	8.0%	7.2%	10.9%	10.0%
$Y_{2\text{-B},f}$ (%)	5.8%	3.8%	8.3%	6.9%

Note. $Y_{i,j}$, Yield of the component j during the initial stages of the reaction. $Y_{f,j}$, Yield of the component j during the final stages of the reaction. $S_{i,j}$, Selectivity of the component j during the initial stages of the reaction. $S_{f,j}$, Selectivity of the component j during the final stages of the reaction. X_i, Initial conversion. X_f = Final conversion. $W = 10–12$ mg; $T = 525$°C; Flow rate = 48–52 cc/min; Feed = 1% 1-Butene/0.7% O_2, the final values are usually after an hour of reaction.

TABLE 3

Comparison of Some other Manganese Oxides

	System			
Y, S, X	Fe–OMS-1	Cu–OL-1	MnO, pure	AMO (MnO_x)
X_i (%)	23.7%	34.9%	16.0%	27.7%
X_f (%)	22.1%	29.7%	14.0%	19.2%
$S_{1,3\text{-B},i}$ (%)	17.9%	16.9%	24.7%	20.5%
$S_{1,3\text{-B},f}$ (%)	17.0%	17.8%	26.6%	15.4%
$S_{2\text{-B},i}$ (%)	21.5%	41.3%	0.0%	26.1%
$S_{2\text{-B},f}$ (%)	20.8%	34.1%	0.0%	16.8%
$Y_{1,3\text{-B},i}$ (%)	4.2%	5.9%	3.9%	5.7%
$Y_{1,3\text{-B},f}$ (%)	3.8%	5.3%	3.7%	3.0%
$Y_{2\text{-B},i}$ (%)	5.1%	14.4%	0.0%	7.2%
$Y_{2\text{-B},f}$ (%)	4.6%	10.1%	0.0%	3.2%

Note. $W = 10–12$ mg; $T = 525$°C; Flow rate = 48–52 cc/min; Feed = 1% 1-Butene/0.7% O_2.

MnO, and Cu^{2+} exchanged with OL-1 (octahedral layered precursor to the OMS-1 and OMS-2) are shown in Table 3. The important observation here is that OL-1 (with Cu), Fe–OMS-1, and amorphous manganese oxide (AMO, MnO_x), upon reduction, transform into a phase which is predominantly MnO (Fig. 5). However, the final reaction products and their selectivities are different from the experiments done with pure MnO. The selectivity toward 2-butenes varies from 34 to 16.8% in the other three catalysts, whereas pure MnO shows virtually no isomerization. Steady state kinetic data for framework substituted [Cu]–OL-1 and [Cu]–OMS-1 are shown in Figs. 6 and 7, respectively.

The layered material, OL-1, contained some Mg^{2+} doped in the framework octahedra with the Cu^{2+} located between the layers. The Cu–OL-1 was found to exhibit higher conversions than the other three systems listed in Table 3, although it has a tendency to be more selective toward isomerization to 2-butenes. Changes in the structure of [Cu]–OMS-1 are evident from XRD data of Fig. 8.

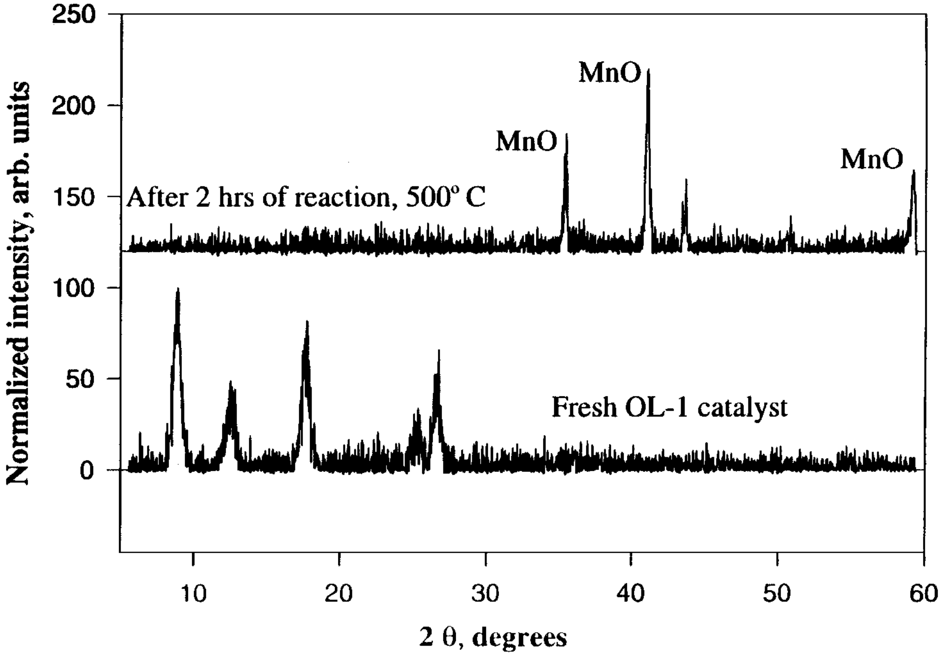

FIG. 5. X-ray powder diffraction–Ion-exchanged Cu–[Mg] OL-1: Change of structure with reaction at 500°C.

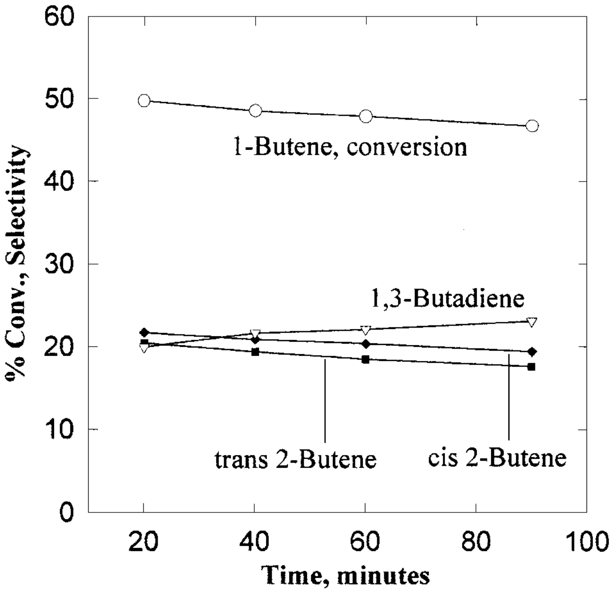

FIG. 6. Steady state kinetics with 1% 1-butene/1.1% O_2/Ar feed. $T = 500°C$. $W = 19.8$ mg. $Q = 40$ cc/min. Catalyst: [Cu]–OL-1.

Table 4 shows another set of systems with copper and iron and their comparison with Fe–OMS-2 and Cu–OL-1. The flow rates of the feed have been decreased to about 40 cc/min and the weight of the catalyst increased to about 20 mg in order to increase the contact time and work at higher conversions. The three new catalysts used in this exercise ([Cu]–OL-1, [Cu]–OMS-1, and [Fe]–OMS-1), have a common feature, the fact that the Cu^{2+} and Fe^{3+} have been doped into the framework during preparation.

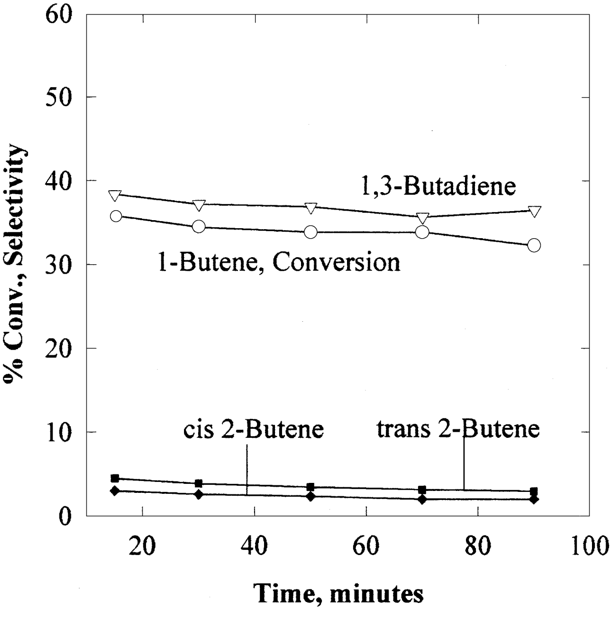

FIG. 7. Steady state kinetics with 1% 1-butene/1.1% O_2/Ar feed. $T = 500°C$. $W = 20.4$ mg, $Q = 40$ cc/min. Catalyst: Fresh [Cu]–OMS-1.

TABLE 4

Comparison of Newer Ion-Exchanged/Framework Substituted Materials

System	% Conv., X_f	Y (1,3-B), %	S (1,3-B), %	S (2-B), %	S, CO_2, %
Cu–OL-1[a]	35.8	5.2	14.6	30.4	55%
[Cu]–OL-1[b]	46.7	10.8	23.1	37	40%
[Cu]–OMS-1[c]	32.3	11.8	36.5	5	58.5%
[Fe]–OMS-1[d]	30	7.5	24.6	12	63.4%
Fe–OMS-2[e]	33.8	6.8	20	21	59%

Note. $W = 20$–22 mg; $T = 525°C$; Flow rate = 40–42 cc/min; Feed = 1% 1-Butene/1.1% O_2 (final values of conversion, yield and selectivity are enclosed).

[a] 17.7% Cu.

[b] 13.7% Cu.

[c] 13.2% Cu.

[d] 2.89% Fe.

[e] 9.56% Fe.

[Cu]–OL-1 shows a very high overall conversion, i.e., 47% with a butadiene yield of about 10.8%. The selectivity toward formation of 1,3-butadiene is about 23% and 37% toward 2-butenes. These figures may be compared with the data for Cu–OL-1 (Table 4, where the Cu^{2+} clearly resides outside the framework). The latter system only exhibits an overall conversion of 36%, a yield of 5.2% for 1,3-butadiene, and a selectivity of 14.6% toward 1,3-butadiene. A comparison of the two systems shows that the [Cu]–OL-1 yields CO_2 with about 40% selectivity whereas Cu–OL-1 yields CO_2 with 55% selectivity. In both cases, phase transformation to a predominantly MnO phase occurs within 40 min of reaction.

The [Cu]–OMS-1 and the [Fe]–OMS-1 both have cations substituted in the framework, although there is still considerable difference in the yield and selectivity for both materials. The selectivity to 1,3-butadiene is as high as 36.5% for [Cu]–OMS-1, the highest observed for any OMS/OL system investigated so far. The yield for 1,3-butadiene is about 11.8%, again, the highest obtained so far. The isomerization reaction is curbed severely, in this case, with the selectivity toward 2-butenes being 5% or lower. Due to there being no isomerization, the overall selectivity toward CO_2 is 58.5%. The [Fe]–OMS-1 system shows lower yield and selectivity toward 1,3-butadiene than [Cu]–OMS-1. In light of our optimization study, the inherent selectivity of [Cu]–OMS-1 and [Cu]–OL-1 toward 1,3-butadiene is the highest observed so far among the systems investigated. The correlation of the isomerization process with the formation of CO_2 under different conditions has been discussed in the next section.

The results of variation of oxygen content in the feed upon the yield, conversion, and selectivity of 1,3-butadiene and 2-butenes in Fe–OMS-2 (representative case) are shown in Tables 5a and 5b. Although the higher the oxygen in the feed, the higher the yield of 1,3-butadiene, the

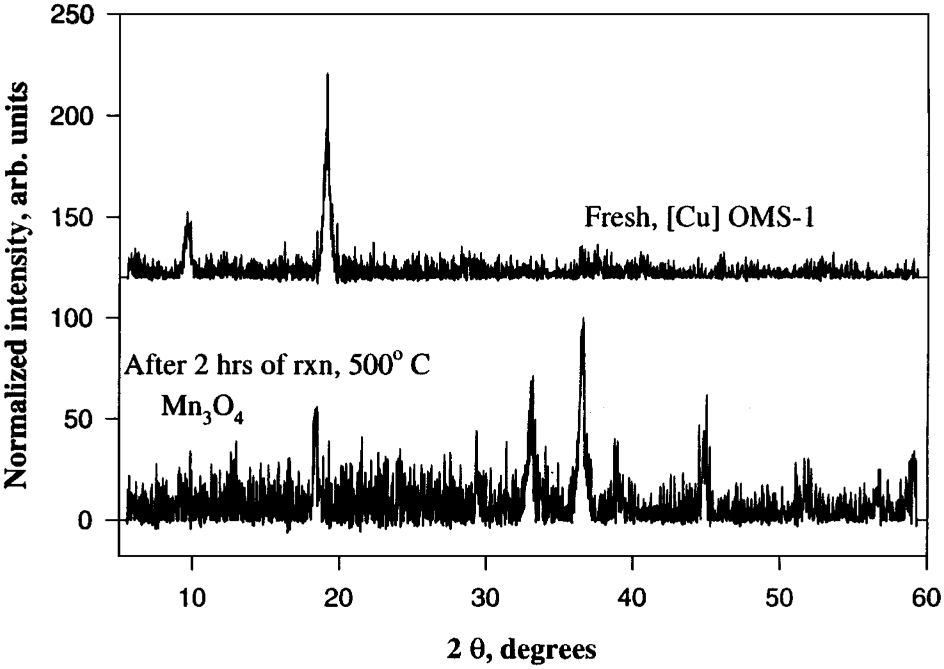

FIG. 8. X-ray powder diffraction–framework substituted [Cu]–OMS-1: Change of structure with reaction at 500°C.

selectivity of the latter has a tendency to drop (there is a tendency to form more CO_2 and water with increased oxygen in the feed). The overall conversion has increased with higher oxygen contents in the feed. The selectivity toward isomerization diminished with increased oxygen in the feed.

Tables 5a and 5b show the effect of oxygen content on the yield and selectivity toward 1,3-butadiene and 2-butenes for Cu–OL-1, [Cu]–OL-1, and [Cu]–OMS-1. For the Cu–OL-1 catalyst, an optimal oxygen content (that which gives the highest selectivity toward the 1,3-butadiene formation) is between 1 and 2% and gives conversions of about 40% and selectivities of about 14.6% toward 1,3-butadiene. The yields and selectivities toward 2-butenes decrease drastically with increase in oxygen content in the feed, as shown in Tables 5a and 5b.

For the [Cu]–OL-1 system, the optimal feed oxygen content is about 2%. At this concentration of oxygen in the feed the overall conversion is about 50%, the selectivity toward 1,3-butadiene is about 26%, and the yield is about 13%. However, at these conditions, isomerization is clearly diminished (Tables 5a and 5b). This means that the selectivity of CO_2 formation is almost as high as 70% at the existing feed conditions.

The effect of feed oxygen on the yield and selectivity of the [Cu]–OMS-1 system toward 1,3-butadiene has also been shown in Tables 5a and 5b. A feed oxygen content of about 1.1% seems to be optimal regarding the selectivity toward 1,3-butadiene.

Figure 9 shows a comparison of the TPR spectra with a stream of 5% CO–He for the 2 catalysts—Cu–OMS-2 (which shows high deactivation and poor selectivity to 1,3-butadiene) and [Cu]–OMS-1 (highest selectivity to 1,3-butadiene, low deactivation, and limited phase change). A migration of the lattice oxygen peak (in the case of [Cu]–OMS-1) by about 40°C from about 405 to about 445°C was clearly observed.

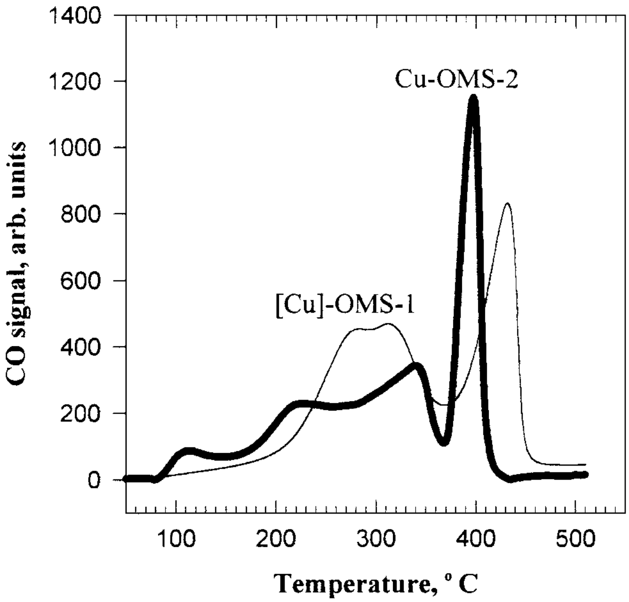

FIG. 9. Temperature programmed reduction, 5% CO/He, Comparison of OMS-2 and OMS-1.

TABLE 5

Effect of Variation of Oxygen Content in the Feed Stream upon the Selectivity, Yield and Conversion (all Final Values, after 1–1.5 h of reaction) of the Selective and Nonselective Oxidation (Except for Fe–OMS-2, all Catalysts Weigh 19.8 mg and Feed Flow Rate Is about 40–42 cc/min. In Case of Fe–OMS-2, Catalyst Weigh 12.7 mg, Feed Flow Rate Is about 46 cc/min)

Product	Catalyst	0% O_2	0.7% O_2	1.1% O_2	2% O_2	3% O_2
A. Selectivity						
2-C_4H_8	Fe–OMS-2	—	35%	20%	10%	—
1,3-C_4H_6	“	—	22%	20%	19%	—
CO_2	“	—	43%	60%	71%	—
Conversion	“	—	30%	33%	43%	—
2-C_4H_8	Cu–OL-1	98%	—	30%	11%	4%
1,3-C_4H_6	“	3%	—	15%	14%	10%
CO_2	“	0%	—	55%	75%	86%
Conversion	“	36%	—	36%	42%	55%
2-C_4H_8	[Cu]–OL-1	—	—	37.5%	8%	4%
1,3-C_4H_6	“	—	—	23%	26%	17%
CO_2	“	—	—	39.5%	66%	79%
Conversion	“	—	—	47%	50%	63%
2-C_4H_8	[Cu]–OMS-1	—	—	5%	<1%	0
1,3-C_4H_6	“	—	—	36.5%	26%	18%
CO_2	“	—	—	58.5%	74%	82%
Conversion	“	—	—	32.3%	40%	49%
B. Yield						
2-C_4H_8	Fe–OMS-2	—	10.5%	6.6%	4.3%	—
1,3-C_4H_6	“	—	6.6%	6.6%	8%	—
Conversion	“	—	30%	33%	43%	—
2-C_4H_8	Cu–OL-1	35%	—	11%	4.6%	2%
1,3-C_4H_6	“	~1%	—	5.4%	6%	5.5%
Conversion	“	36%	—	36%	42%	55%
2-C_4H_8	[Cu]–OL-1	—	—	18%	4%	2.5%
1,3-C_4H_6	“	—	—	11%	13%	10.7%
Conversion	“	—	—	47%	50%	63%
2-C_4H_8	[Cu]–OMS-1	—	—	1.6%	<1%	~0
1,3-C_4H_6	“	—	—	11.8%	10.4%	8.8%
Conversion	“	—	—	32.3%	40%	49%

DISCUSSION

Oxidative Dehydrogenation without Feed Oxygen–Cu-OMS-2

Figure 1 shows that the oxygen from the lattice and other chemisorbed species are consumed rapidly with 40 min of the reaction. The selectivity of 1,3-butadiene has gone down to about 3–4% as expected, and from the carbon balance, it is clear that the formation of CO_2 is negligible at higher times. The only reaction proceeding is that of isomerization which yields *cis* and *trans*-2-butenes. The selectivities add up to 100%, and the error resulting from the final carbon balance corresponds roughly to the error in the measurement of 2-butenes, i.e., about 5–7% relative to values of conversions and selectivites that are reported. Since the selectivity of isomer formation is nearly 100%, there is very little cracking or coking or any other side reaction occurring, other than the following reactions:

$$C_4H_8 + 0.5\,O_2 \rightarrow C_4H_6 + H_2O \qquad \text{...............} \; R2$$

$$C_4H_8 + 6\,O_2 \rightarrow 4\,CO_2 + 4\,H_2O \qquad \text{...............} \; R3$$

$$C_4H_8 \rightarrow 2\text{-}C_4H_8 \qquad \text{...............} \; R4$$

Oxidative Dehydrogenation with Cu–OMS-2 at Different Temperatures

Each experiment has been done by using a fresh sample of catalyst and the feed contains 0.7% oxygen along with 1% 1-butene (Fig. 2, Table 1). Isomerization appears to be enhanced by higher temperature. The feed being substoichiometric (for total oxidation) and slightly more than stoichiometric for partial oxidation would indicate that almost all the feed oxygen is being consumed in the process. In our preliminary experiments, we have used high temperatures and catalyst weights of about 40 mg subjected to feed flow rates of about 26 cc/min. We speculate that bed effects are playing a role in this experiment. This matter is analyzed and discussed in the next subsection.

Deactivation was found to occur despite the presence of oxygen in the feed although the 1,3-butadiene production was sustained despite the deactivation. The final values of 1,3-butadiene selectivity after about 1–1.5 h of reaction are shown in Table 1. The selectivity toward CO_2 decreased at higher temperature and corresponded to the increase in isomerization. In all these cases, a phase change to a mixture of Mn_3O_4 and MnO occurred as shown in the XRD pattern of Fig. 3 and this can explain the rapid deactivation. The final values of the products do not correlate with the “molecular sieve,” microporous catalyst with which we started, but are more characteristic of the activity of the resultant mixed oxide phase that formed. The deactivation observed in the form of reduction of overall conversion and yield/selectivity to 1,3 butadiene appears to indicate that we would have been able to generate a more active catalyst had the structural integrity of the starting catalyst been retained. By using high feed oxygen concentrations of over 5%, the structure was retained for longer times of over 4–5 h but with over 90% selectivity to combustion products.

Ion-Exchanged OMS-2, OMS-1, and OL-1 as Catalysts for Oxidative Dehydrogenation

After investigating the Cu–OMS-2 system the MnO/Mn_3O_4 phase formed very quickly leading to considerable uncertainty in making any kind of measurements regarding the quantification of active sites or the calculation of any thermodynamic data. A way to structurally modify the catalyst and prevent the rampant phase transformation was therefore necessary.

Three batches of OMS-2 (Hollandite type) catalysts were ion-exchanged with K^+, Cr^{3+}, and Fe^{2+}, respectively, and the kinetic data were compared with Cu^{2+} exchanged OMS-2 (Table 2). Although the Fe–OMS-2 showed higher yield and selectivity toward 1,3-butadiene production, there was very little improvement in selective oxidation. Ion-exchanged OMS-2 is not capable of changing the redox properties of the as-synthesized catalyst and therefore ineffectual in its capability to selectively oxidize 1-butene.

The phase change to MnO occured within 30 min of reaction. These experiments were done with lower catalyst loading, about 12 mg, which was spread very thin, with much lower aspect ratios (refer to the Experimental section) than those in Figs. 1 and 2 to minimize non-uniformity in the catalyst bed. The deactivation of Cu–OMS at 525°C in comparison with Table 1 is lower. The overall conversion dropped from 24.3 to 20.9% when a thin layer of catalyst was used as opposed to from 31.1 to 25.2% in Table 1. The selectivity of 2-butenes measured in Table 1 was 47.9% after 1.5 h of reaction, whereas in Table 2, it is only about 28%. The butadiene selectivity remains similar, i.e., about 17–18%, despite changes in the feed flow rate and catalyst weight. Clearly, the rate of deactivation brought about by phase change is a function of the flowrate/bed weight ratio. Subsequent experiments have been carried out under conditions with minimal bed effects, but given the volume of the microreactor (about 0.75 mL), it is not possible to operate at too high a flow rate nor is it possible to work with catalysts smaller than 10 mg in weight, which might produce minimal conversions and yields. Therefore, we have had to strike an optimal balance and work in a regime where external mass transfer may be a problem, just so that we obtain reasonable values of yields of 1,3-butadiene and 2-butenes, with minimal errors in measurements.

For ion-exchanged OMS-1, as shown in Table 3, the yields toward 1,3-butadiene and 2-butenes are even lower than before and so is the overall conversion. Phase changes to MnO were also observed in Fe–OMS-1 as in the previous cases. Amorphous manganese oxide, AMO (a mixture of manganese oxide phases), which showed no appreciable peaks in the XRD data was also tried as catalyst. The high deactivation and very poor selectivity in oxidation (Table 3) were again negative factors, although AMO has been found to be effective in the photocatalysis of methyl bromide (12). The resultant phase upon reduction is once again MnO. This may be compared with pure commercial MnO as a catalyst. The difference is that in the case of commercial MnO, there is small deactivation, low overall conversion, and higher selectivity toward 1,3-butadiene as compared to the previous cases, but absolutely no isomerization. The possibility of generating acid sites with the ion-exchange process could make the OMS system different from pure commerical MnO.^{R} If acidity has been induced, then it must be very weak, because, the formation of iso-butylene does not occur in any of these cases. Structurally, there is no difference in the MnO formed by phase transformation and commercial MnO. Even if there are differences in the surface areas of the two materials, that would not change the chemical nature of the active sites. More detailed experiments are underway to measure and characterize the acidity of these catalysts prior to and after the reduction process.

The kinetic data obtained by the use of the octahedral layered material, OL-1, are shown in Tables 3 and 4. The OL-1 starting materials previously ion-exchanged with Cu^{2+} formed MnO after reduction with the appropriate initial deactivation. The large extent of isomerization and high conversion made it different from Fe–OMS-1 or AMO under the same conditions (Table 3). The comparison of these three systems is important because exactly the same conditions have been used to carry out kinetics and the resulting deactivation leaves MnO as a final product.

Framework Substitution in the Octahedra

The ion-exchanged OMS materials (studied in the previous section) have the cations placed, usually within the tunnel structure (1–3). Upon reduction and the ensuing collapse of the tunnel structure the cations could form oxides and exist as impurities with possible catalytic activity. Framework substitution of the manganese from the octahedra on the other hand could clearly influence the release of oxygen from the lattice. According to Kung's analysis for orthovanadates (11), the selective substitution of a more reducible cation with a cation of lower reducibility serves to make it less likely to release oxygen from such sites. This implies that the catalyst is more selective in its capacity to oxidize (11). From Kung's analysis and experimental data for *n*-butane oxidation by orthovanadate catalysts with framework substituted cations of different reduction potential (11), one would be inclined to believe that the substitution of manganese in the octahedra of our OMS/OL systems by other cations could alter the reducibility of the catalyst. Similarly, if the substituted OMS lost less oxygen then the tunnel structure could be stabilized. Two such systems where copper is substituted in the framework have been investigated ([Cu][Mg]–OL-1 and [Cu]–OMS-1).

Similar samples to the one studied here have been characterized by techniques such as TEM, FTIR, and X-ray absorption, which confirm the local framework environment of the copper (16). Steady state data show a marked increase in the selectivity toward 1,3-butadiene in the case of [Cu]–OMS-1 (36.5%, Table 4, Fig. 7) in comparison to any other catalytic system investigated in this work. The yield toward 1,3-butadiene is about 11.8% and is slightly more than what is obtained for [Cu]–OL-1 (Table 4, Fig. 6). The latter is also a framework-exchanged material and shows considerable conversion (46.7% with 10.8% yield toward 1,3-butadiene but also shows 37% selectivity to the 2-butenes) under the same reaction conditions. The difference in the two materials appears to be that isomerization occurs with [Cu]–OL-1.

The fact that isomerization occurs strongly in the OL-1 catalyst is amply demonstrated in both kinds of OL-1 used in this paper, framework exchanged Cu–OL-1 and ion-exchanged Cu–OL-1 (refer to Tables 3 and 4). The important structural differences leading to deactivation of the two types of framework-substituted catalysts are that upon undergoing reduction, the [Cu]–OL-1 transforms to a MnO phase (similar to Fig. 5) whereas the [Cu]–OMS-1 system transforms to Mn_3O_4 (Hausmannite, Fig. 8).

The TPR data shown in Fig. 9 are a measure of the ease or the difficulty with which oxygen is liberated from the catalyst of interest under reducing conditions. In a typical transition metal oxide catalyst three peaks are usually observed, corresponding to weakly held and/or physisorbed oxygen, chemisorbed oxygen (usually O^-), and lattice oxygen or oxygen coordinated with the metal (O^{2-}), at progressively higher temperatures. From the analysis of Iwamoto *et al.* (13) and Kung *et al.* (14) the ease of release of lattice oxygen usually determines the selectivity of the oxidation process. The lower the temperature of the third peak, the lower the selectivity of the catalyst toward partial oxidation. Figure 9 shows that the lattice oxygen peak for [Cu]–OMS-1 is about 40°C higher than that for Cu–OMS-2. This indicates that framework substituted OMS-1, which showed the highest selectivity toward the formation of 1,3-butadiene, also exhibits more stability toward reduction. The shift in the lattice oxygen peak confirms this and serves to complement the finding that the resultant phase is Mn_3O_4 alone.

The [Cu]–OL-1 provides oxygen at lower temperatures (temperature programmed reduction experiments with CO–He) which could explain the higher conversions achieved in comparison to [Cu]–OMS-1. This could also explain the change of phase all the way to MnO for [Cu]–OL-1 whereas [Cu]–OMS-1 (which is less active but more selective to 1,3-butadiene) is transformed to only Mn_3O_4.

It may be asked why Cu–OMS-2, which was earlier shown to transform into a MnO/Mn_3O_4 phase, should be less selective toward 1,3-butadiene than [Cu]–OMS-1, which exhibits the same phase change upon reduction. The answer may lie in the average oxidation state of the manganese in the original starting material. The formula for the starting OMS-2 material is TMn_8O_{16}. The average oxidation state of manganese is 3.875. The general formula for OMS-1 has been experimentally determined to be the following:

$$Mg^{2+}_{0.98-1.35}Mn^{2+}_{1.89-1.94}Mn^{4+}_{4.38-4.54}O_{12}\cdot\ 4.47\text{–}4.55\ H_2O^{R}$$

The average oxidation state may be evaluated to be about 3.5, which is lower than OMS-2. The overall deactivation for OMS-1, therefore, would be smaller than the case for ion-exchanged OMS-2 catalysts because of the larger magnitude of change in the oxidation state.

Mechanisms for Phase Change and for the Reaction

The phase change of a good partial oxidation catalyst ought to be reversible. According to the original mechanisms proposed by Mars and van Krevelen (15) and reviewed by Kung (14), the oxidation catalysis occurs by a redox process. This would imply the following scheme:

$$A \overset{1}{\leftrightarrow} B \underset{2}{\rightarrow} C \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{R5}$$

The transformation of A to B and back to A is critical for a partial oxidation process, whereas the transformation of phase B to C is undesirable. This is only possible if $\Delta G_{\text{A-B}}$ is small compared to $\Delta G_{\text{B-C}}$. Kung *et al.* (14) in their review article have discussed this case for Fe_2O_3 (A), Fe_3O_4 (B), and FeO (C). A parallel may be drawn in our system here and illustrated as follows:

$$\text{OMS-1,2/OL-1} \xrightarrow{1} Mn_3O_4 \xrightarrow{2} MnO \qquad \ldots\ldots\ldots \text{R6}$$

Unfortunately, in our system, ΔG_1 seems to be fairly high so as to rapidly cause a transition to Mn_3O_4 and in some cases a transformation all the way to MnO.

In a review describing the competing processes of partial and total oxidation of 1-butene on ferrites, Kung *et al.* (14) have proposed a dual site mechanism for this reaction. The selective oxidation sites result in the formation of an intermediate which eventually is converted to 1,3-butadiene whereas intermediate species forming on other sites lead to combustion (total oxidation). If oxygen is in surplus in the feed, then it can oxidize the intermediates that eventually form 1,3-butadiene and 2-butenes (14).

Some of our observations are consistent with the above mechanism, notably the decrease in isomerization selectivity with increased oxygen content in case of all the systems studied (refer to Tables 5a and 5b). The large increase in 1,3-butadiene selectivity, observed for the [Cu]–OMS-1 system is likely due to substitution of the cation in the framework of the OMS-1 octahedra. This type of substitution holds the key to the stabilization of these structures and selective generation of more value-added products like 1,3-butadiene.

CONCLUSIONS

The OMS materials have been synthesized as microporous structures but owing to lack of stability under reducing conditions, they cannot sustain their high capacity to release oxygen on a continuous basis. Replenishment of oxygen was enhanced by using higher feed oxygen content, but that (in spite of stabilizing the structure) resulted in extremely unselective oxidation. The results of the reactions and the accompanying phase changes indicate that the microporous nature of the OMS materials with its 4.6 Å (OMS-2) and 6.9 Å (OMS-1) size tunnels, have not been effectively utilized yet. The stability of the catalyst is a stumbling block in this endeavor.

Experiments with commercial ferrites (widely used in the industry) show an overall conversion of about 61%, a 1,3-butadiene yield of 38%, and a selectivity of about 65%. Our best partial oxidation catalyst, [Cu]–OMS-1, shows an overall conversion of only 32%, a 1,3-butadiene yield of 11.5–12% and selectivity toward butadiene of about 36%. Use of OMS materials at higher temperatures may be restricted in certain reactions due to phase changes. However, there is potential for using OMS as low temperature oxidation catalysts.

The object of exploring the behavior of such a system under the influence of a feedstock such as 1-butene is to be able to synthesize a suitable catalyst which will eventually give the desired properties. The roles of several parameters have been identified in the course of this work. The 1-butene/oxygen content in the feed stream, temperature, and catalyst properties such as substitution of dopant cations are important. The most important aspect of this research is that substitution of framework manganese with copper has resulted in a marked rise in selectivity to 1,3-butadiene (from about 15–20% in the case of ion-exchanged materials to about 36% for the framework exchanged materials). Ion-exchanging the free cation in the as-synthesized catalyst does not seem to influence the catalytic properties significantly. Framework substitution with several cations with varying reduction potential needs to be done in order to demonstrate this behavior on a statistical level.

The potential of OMS in releasing oxygen at lower temperatures has been very good. OMS has been found effective in the oxidative dehydrogenation of alchohols, the oxidation of carbon monoxide, and the oxidative dehydrogenation of cyclohexane to cyclohexene. The 1-butene environment provides a harsher test to the thermal stability under reducing conditions, because, the 1,3-butadiene reaction takes place, negligibly, at temperatures below 350°C. The results of our study, therefore, show that controlling the phase change by framework substitution in the octahedra is one of the important parameters which influence the selective oxidation of 1-butene to 1,3-butadiene.

Further work in synthesis, characterization, and catalysis is underway in our research group with the goal of generating more thermally stable catalysts and an optimal system which can combine the advantages of high surface area with higher activity and selectivity toward partial and total oxidation.

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