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Journal of Catalysis 250 (2007) 365–368

JOURNAL OF CATALYSIS

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Research Note

Catalytic oxidation of ethylene and ethane to formaldehyde by oxygen

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Received 8 May 2007; revised 5 June 2007; accepted 12 June 2007

Abstract

The selective oxidation of ethylene by oxygen produced formaldehyde with a single-pass yield of ∼30% at a temperature of 863 K and a contact time of 0.08 $\mathrm{s\,g\,cm^{-3}}$ over a mesoporous silica (SBA-15)-supported molybdenum oxide catalyst. Oligomeric MoO_x species and polymeric MoO_x clusters were responsible for this reaction. The exploitation of a double-bed catalytic reaction mode containing Dy_2O_3–Li^+–MgO–Cl^- and MoO_x/SBA-15 as the upstream, and the downstream catalysts converted ethane directly to formaldehyde by oxygen with a single-pass yield of 14% at 863 K.

Keywords: Ethane; Ethylene; Selective oxidation; Formaldehyde; Molybdenum oxide; Mesoporous silica

1. Introduction

The use of lower-alkane resources, particularly methane and ethane, for the production of valuable chemicals is one of the most challenging research areas in catalysis. Numerous heterogeneous catalysts have been reported for the partial oxidation of methane or ethane to organic oxygenates, such as formaldehyde, acetaldehyde, and acetic acid, but single-pass yields to any of these oxygenates barely exceed 5% [1–6]. Formaldehyde, one of the world's most important chemical products, is currently manufactured via a three-step process comprising high-temperature steam reforming of methane to syngas, methanol synthesis from syngas, and selective oxidation of methanol. This multistep process is costly and energy intensive. A novel route of direct conversion of the cheap, abundant lower alkanes to formaldehyde would be highly attractive.

In a recent paper [7], we reported that SBA-15 (a typical mesoporous silica)-supported molybdenum oxides could catalyze the formation of HCHO with a yield of ∼4% in the selective oxidation of C_2H_6 by O_2 at 873 K. The work also indicated that HCHO was likely produced via the consecutive oxidation of C_2H_4 by O_2 by

$$C_2H_4 + O_2 \rightarrow 2HCHO. \quad (1)$$

To the best of our knowledge, there have been no reports on the direct conversion of C_2H_4 to HCHO via catalytic oxidation before our work. One purpose of this work is to clarify the catalyst requirements and the possible reaction scheme for this new catalytic reaction. Moreover, because this reaction occurs at 823–873 K, at which the oxidative dehydrogenation of C_2H_6 to C_2H_4 by O_2 also can occur efficiently [8], it may be possible to develop a double-bed catalytic reaction route for the direct conversion of C_2H_6 to HCHO with a higher single-pass yield. The present paper reports the efficient formation of HCHO via the catalytic oxidation of C_2H_4 over MoO_x/SBA-15 catalysts and via the novel double-bed catalytic oxidation of C_2H_6.

2. Experimental

SBA-15 and SBA-15-supported molybdenum oxides were prepared according to the procedures that we described previously [7]. The Mo content (expressed using the wt% of MoO_3) in each sample was determined by ICP measurements. Catalytic reactions were carried out in a fixed-bed quartz reactor operated at atmospheric pressure. In the single-bed reaction mode, the catalyst was loaded into the middle of the hot zone of the quartz reactor. The double-bed reaction mode comprised an upstream catalyst, Dy_2O_3–Li^+–MgO–Cl^-, prepared as described previously [9], and a downstream catalyst, MoO_x/SBA-15. Both cat-

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doi:10.1016/j.jcat.2007.06.015

alysts were located in the temperature-homogeneous hot zone of the reactor, and they were separated with a thin layer of quartz wool. After pretreatment with O_2-containing gas flow at 873 K, the reactant gas mixture containing C_2H_4, O_2, and N_2 (or C_2H_6, O_2, and N_2) was introduced into the reactor at an appropriate temperature, with N_2 used for dilution. The products were analyzed by online gas chromatography as described previously [7]. Generally, the carbon balance was >90%.

3. Results and discussion

Fig. 1 shows the catalytic results for the oxidation of C_2H_4 by O_2 at 848 K over the MoO_x/SBA-15 catalysts with different Mo contents. No reaction occurred over SBA-15 alone, and C_2H_4 conversion increased significantly with increasing the Mo content up to 20.1 wt%. Although HCHO was formed over the catalysts with a lower Mo content (⩽6.6 wt%), the selectivity of CO was even higher than that of HCHO over these catalysts. CH_3CHO also was formed at this time, with a selectivity of ∼20%. When the Mo content was increased from 6.6 to 9.5 wt%, the selectivity of both CO and CH_3CHO decreased significantly, and that of HCHO increased steeply. Further increases in the Mo content did not change the product distributions significantly. The highest yield to HCHO was obtained over the 20.1 wt% MoO_x/SBA-15 catalyst.

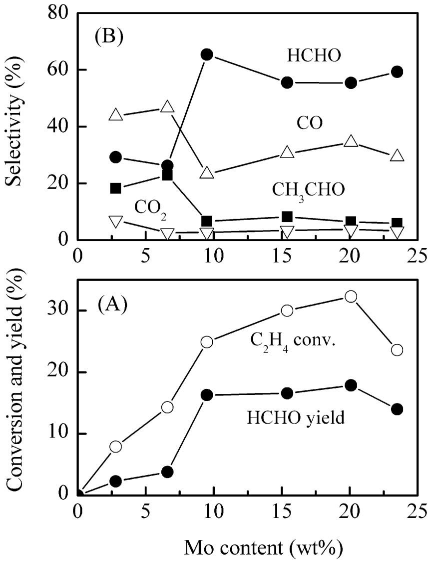

Fig. 1. Dependence of catalytic behavior of the MoO_x/SBA-15 catalysts on Mo content for selective oxidation of ethylene by O_2. Reaction conditions: $T = 848$ K, $W(\text{catalyst}) = 0.1$ g, $P(C_2H_4) = P(O_2) = 10.1$ kPa, $F = 150\ \text{ml min}^{-1}$.

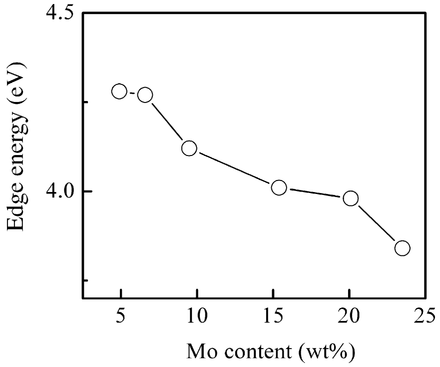

Fig. 2. Dependence of edge energy for the MoO_x/SBA-15 catalysts after the selective oxidation of ethylene by O_2 on Mo content.

In previous work, we characterized the MoO_x/SBA-15 catalysts with different Mo contents by various techniques, including XRD, N_2-sorption, Raman, H_2-TPR, UV–vis, SEM, and TEM, and reported the results [7]. In brief, the samples with lower Mo content (⩽4.9 wt%) contained mainly monomeric MoO_x species, and an increase in Mo content to 9.5 wt% caused the formation of oligomeric MoO_x species and polymeric MoO_x clusters in the mesoporous channels of SBA-15. The increase in Mo content to ⩾15.4 wt% led to the growth of MoO_x species into 10–20 nm MoO_x nanoparticles and resulted in the unlinking of the silica wall of SBA-15. A further rise in Mo content to 23.5 wt% caused the appearance of a large number of needle-like MoO_3 crystallites. In this work, we performed diffuse reflectance UV–vis spectroscopy measurements for the MoO_x/SBA-15 samples after the catalytic oxidation of C_2H_4 by O_2. As shown in Fig. 2, the edge energy (E_g) for the low-energy charge-transfer transition calculated from the UV–vis spectra with the method proposed by Weber [10] decreased significantly as the Mo content rose to >6.6 wt%. This indicates the change in MoO_x domains from monomeric species (E_g, ∼4.3 eV) to polymeric clusters [10]. This decrease in the E_g value corresponds well to the steep rises in HCHO selectivity and yield shown in Fig. 1. Therefore, the oligomeric MoO_x species and polymeric MoO_x clusters are likely responsible for the selective oxidation of C_2H_4 to HCHO by O_2, whereas the monomeric MoO_x species produce CO and CH_3CHO with higher selectivity in addition to HCHO.

To gain insight into the reaction scheme for HCHO formation, we have investigated the effects of various kinetic factors on product selectivities as well as C_2H_4 conversions over the 20.1 wt% MoO_x/SBA-15 catalyst (see Supplementary material, Figs. S1–S3). From the temperature dependence of C_2H_4 conversion, the apparent activation energy was calculated to be 290 kJ mol^{-1}, lower than that (350 kJ mol^{-1}) for the oxidation of C_2H_6 over the same catalyst [7]. An HCHO selectivity of >70% could be obtained at lower temperatures, and an HCHO yield of >30% were obtained at ⩾863 K, where HCHO selectivity could be maintained at >60% (Fig. S1). The specific rate for HCHO formation was 63.1 mmol g^{-1} h^{-1} or 45.2 mol mol Mo^{-1} h^{-1} at 863 K over the 20.1 wt% MoO_x/SBA-15 catalyst. Lower O_2 pressure and shorter pseudo-contact time (expressed as the ratio of catalyst weight to total flow rate, W/F) also favored the selectivity of HCHO (Figs. S2 and S3). These observations suggest that the consecutive oxidation of HCHO to CO occurs at higher temperatures or O_2 partial pressures, or at longer contact times. CH_3CHO was also formed, but the highest selectivity of CH_3CHO was only ∼20% at the lowest temperature or the shortest contact time investigated.

As we mentioned earlier [7], HCHO might be formed via a CH_3CHO intermediate but not directly from C_2H_4 oxida-

Table 1
Product distributions for the oxidation of CH_3CHO by O_2 over the 20.1 wt% MoO_x/SBA-15 catalyst[a]

Temperature (K)	W/F ($s\,g\,cm^{-3}$)	CH_3CHO conversion (%)	Selectivity[b] (%)			
			HCHO	CH_4	CO	CO_2
773	0.04	45	34	14	44	4.2
823	0.04	70	37	12	43	6.0
848	0.04	77	34	16	46	6.2
873	0.04	89	30	13	49	6.8
823	0.008	48	25	21	47	3.1
823	0.02	58	31	16	46	3.8
823	0.06	71	36	9.7	45	6.9
823	0.08	74	32	8.6	50	8.0

[a] Reaction conditions: $P(CH_3CHO) = P(O_2) = 3.75$ kPa.
[b] Small amounts of C_2H_6 and C_2H_4 were formed.

tion. The kinetic studies described above cannot completely exclude this possibility. Thus, we have studied the oxidation of CH_3CHO by O_2 over the 20.1 wt% MoO_x/SBA-15 catalyst. We used a reactant gas mixture containing CH_3CHO with a partial pressure comparable to the total concentration of all of the products obtained for the oxidation of C_2H_4. The results summarized in Table 1 reveal that the selectivity of HCHO obtained in the oxidation of CH_3CHO is always <50% even under lower temperatures or at shorter contact times. Moreover, methane, which could not been detected in the oxidation of C_2H_4, also was formed during the oxidation of CH_3CHO. We speculate that the following reactions of CH_3CHO proceed over the MoO_x/SBA-15 catalyst, forming HCHO, CO, and CH_4:

$$CH_3CHO + O_2 \rightarrow HCHO + CO + H_2O \tag{2}$$

and

$$CH_3CHO \rightarrow CH_4 + CO. \tag{3}$$

On the other hand, the oxidation of C_2H_4 by O_2 under similar conditions could provide HCHO with selectivities significantly greater than 50% (Figs. S1–S3). These results allow us to propose that HCHO is a major primary product formed directly from the oxidation of C_2H_4 over the 20.1 wt% MoO_x/SBA-15 catalyst. Friend et al. [11] proposed that the C–C coupling of HCHO to form C_2H_4 on a Mo(110) surface proceeded via an ethylene dialkoxide intermediate detected by IR spectroscopy. Interestingly, the C–C coupling of HCHO is just the reverse reaction of the conversion of C_2H_4 to HCHO. We speculate that the adsorption of C_2H_4 on oligomeric MoO_x species and polymeric MoO_x clusters also may form the ethylene dialkoxide ($-OCH_2CH_2O-$) intermediate, and that the oxidative cleavage of the C–C bond of this intermediate can give HCHO. The lattice oxygen species of the polymeric MoO_x clusters with higher reactivities also may be required for such a conversion.

Fig. 3 shows the stability of the 20.1 wt% MoO_3/SBA-15 catalyst for the selective oxidation of C_2H_4 to HCHO by O_2 at 863 K. In the initial 10 h, no significant decreases in C_2H_4 conversion and HCHO selectivity occurred, and HCHO yield could be maintained at ~30%. The selectivity and yield of HCHO decreased slightly when the time on stream was increased to >10 h. An HCHO yield of ~24% still could be obtained after ~35 h of reaction.

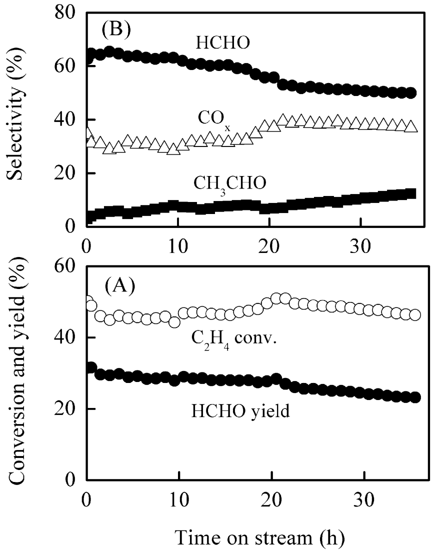

Fig. 3. Changes of catalytic performances with time on stream for the oxidation of ethylene by O_2 over the 20.1 wt% MoO_x/SBA-15 catalyst. Reaction conditions: $T = 863$ K, $W(\text{catalyst}) = 0.2$ g, $P(C_2H_4) = P(O_2) = 10.1$ kPa, $F = 150$ ml min^{-1}.

We developed a double-bed catalytic reaction route for the production of HCHO directly from C_2H_6 by combining the MoO_x/SBA-15 catalyst with a C_2H_6 oxidative dehydrogenation catalyst. Numerous catalysts are known to catalyze the oxidative dehydrogenation of C_2H_6 efficiently [8]. We selected the Dy_2O_3–Li^+–MgO–Cl^- catalyst developed by Lunsford et al. [9] for the present work because the optimum operating temperature range for this catalyst in the oxidative dehydrogenation of C_2H_6 (823–873 K) is almost the same with that for our MoO_x/SBA-15 catalyst in the selective oxidation of C_2H_4 to HCHO. The catalytic results using single- and double-bed reaction modes for the direct oxidation of C_2H_6 by O_2 are summarized in Table 2. With the single Dy_2O_3–Li^+–MgO–Cl^- catalyst, C_2H_4 was produced with a yield of 54% at a selectivity of 83%, but no HCHO was formed. Lunsford et al. [9] reported the formation of a small amount of CH_4 (selectivity ~1%) during the oxidative dehydrogenation of C_2H_6 over the Dy_2O_3–Li^+–MgO–Cl^- catalyst. However, we did not obtain CH_4, possibly because the partial pressures of C_2H_6 and O_2 used in our work were much lower than those used by Lunsford et al. [9]. The single 20.1 wt% MoO_x/SBA-15 catalyst could catalyze the oxidation of C_2H_6 to HCHO by O_2, but the HCHO yield was only 3.1% under the conditions of Table 2. The combination of the Dy_2O_3–Li^+–MgO–Cl^- and the 20.1 wt% MoO_x/SBA-15 catalysts in the same reactor provided an HCHO yield of 13%. Therefore, both the oxidative dehydrogenation of C_2H_6 and the selective oxidation of C_2H_4 to HCHO proceeded smoothly in our double-bed reactor. Table 2 also shows that an appropriate temperature is required to obtain a high HCHO yield, whereas a relatively higher O_2 partial pressure favors the HCHO yield. We obtained an HCHO yield of 14% at an O_2 pressure of 14.2 kPa. To the best of our knowledge, this is the highest single-pass HCHO yield achieved from the catalytic oxidation of CH_4 or C_2H_6 by O_2.

Table 2
Catalytic oxidation of ethane by O_2 with single- and double-bed reaction modes[a]

Catalyst bed[b]	C_2H_6 conversion (%)	Selectivity[c] (%)			HCHO yield (%)
		HCHO	C_2H_4	CO_x	
Single: Catal. A	65	0	83	17	0
Single: Catal. B	11	28	39	25	3.1
Double: Catal. A + Catal. B	63	20	40	38	13
Double: Catal. A + Catal. B[d]	44	23	51	24	10
Double: Catal. A + Catal. B[e]	78	12	38	49	9.6
Double: Catal. A + Catal. B[f]	57	7.0	60	33	4.0
Double: Catal. A + Catal. B[g]	73	19	41	40	14
Double: Catal. A + Catal. B[h]	75	18	39	42	13

[a] Reaction conditions: $T = 863$ K, $P(C_2H_6) = P(O_2) = 10.1$ kPa, $F = 50$ ml min^{-1}.
[b] Catal. A: Dy_2O_3–Li^+–Mg–Cl^- (5.0 g), Catal. B: 20.1 wt% MoO_x/SBA-15 (0.2 g).
[c] The remaining product is acetaldehyde.
[d] $T = 843$ K.
[e] $T = 873$ K.
[f] $P(O_2) = 6.1$ kPa.
[g] $P(O_2) = 14.2$ kPa.
[h] $P(O_2) = 20.3$ kPa.

4. Conclusion

We have shown that ethylene can be efficiently oxidized into formaldehyde by oxygen over the MoO_x/SBA-15 catalyst with a Mo content of ~10–20 wt%. Oligomeric MoO_x species or polymeric MoO_x clusters are the catalytically active species for the selective formation of formaldehyde. It is proposed that formaldehyde is formed as a major primary product from the oxidation of ethylene in parallel to acetaldehyde, which is a minor primary product. Combined with a catalyst effective for oxidative dehydrogenation of ethane to ethylene, this novel reaction gives us the opportunity to produce formaldehyde directly from ethane by oxygen with a yield as high as 14%.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20433030 and 20625310), the National Basic Research Program of China (2005CB221408 and 2003CB615803), the Key Scientific Project of Fujian Province of China (2005HZ01-3), the Programs for New Century Excellent Talents in University of China (NCET-04-0602 to Y.W.) and Fujian Province (grant to Q.Z.).

Supplementary material

The online version of this article contains additional supplementary material.

Please visit DOI: 10.1016/j.jcat.2007.06.015.

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