Catalysis Letters 69 (2000) 199–202

Highly effective molybdena–manganese catalyst for propane oxidative dehydrogenation

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Received 22 February 2000; accepted 14 August 2000

A manganese oxide catalyst impregnated with molybdenum exhibits high yield, productivity and stability in the oxidative dehydrogenation of propane to propene. This catalyst exhibits catalytic activity and yield to propene at temperatures as low as 623 K.

Keywords: Mo–Mn–O catalyst, oxidative dehydrogenation, propane to propene

1. Introduction

Attempts to transform cheap and abundant feedstock and by-products of oil refining processes into more valuable products have recently resulted in great research interest in the oxidative dehydrogenation of propane.

The performance of catalysts for oxidative dehydrogenation is usually described in terms of propane conversion and yield to propene. A wide variety of catalytic systems has been proposed for this reaction, VMgO being the most promising one [1–6]. Recently, a MgMoO system has been reported to be active and relatively selective in the oxidehydrogenation (ODH) of propane to propene [6–10]. In particular, V–Mg–O and Mg–Mo–O systems have been extensively studied in order to identify active phases. In general, the reported initial activity temperatures with yield to propene are usually above 723 K and even higher. Table 1 shows the catalytic behaviour of different systems, based on data published in the literature.

The catalytic process currently in use in industry is catalytic dehydrogenation. In this process, the catalyst is deactivated with time on stream and needs regeneration. Therefore, a suitable way of comparing the performance of catalysts used in different processes is the rate of propene formed per catalyst mass.

In the present work, we study the catalytic behaviour of the Mo–Mn–O system. This system differs from other systems in the facts that it can activate C_3H_8 to C_3H_6 at low temperatures and that CO is practically non-existent among its oxidation products.

2. Experimental

Mn_2O_3 preparation was carried out by calcination of $MnCO_3$ at 873 K for 5 h. The ixMo/Mn_2O_3 catalysts were prepared by dry impregnation. Knowing the pore volume of Mn_2O_3, the concentration of the solution used in each case was such that an amount x (in wt%) of molybdenum could be incorporated in a volume equivalent to that of the Mn_2O_3 pores (in one or more impregnation stages). The corresponding amount of solution was added on the dry

Table 1
Reaction temperature and catalytic activity. Comparison of different catalytic systems.

Catalytic system	Temperature of reaction (K)	$R_{C_3H_6}$ (%)	Reference
YVO_4	773	4.0	[11]
$LaVO_4$	773	2.2	[11]
$CeVO_4$	773	1.7	[11]
$NdVO_4$	773	2.4	[11]
$SmVO_4$	773	7.6	[11]
$EuVO_4$	773	3.4	[11]
V–Mg–O	673	–	[12]
V–Mg–O	773	–	[12]
ALPO-5	813	0.1	[4]
V/ALPO-5	773	10.4	[4]
V/MgO	773	8.0	[4]
V–Mg–O	773	6.0	[2]
V–Si	673	1.9	[13]
V–Al	673	3.0	[13]
V–Ti	673	1.9	[13]
V–Mg	673	3.9	[13]
V–La	673	2.8	[13]
V–Sm	673	2.8	[13]
MoMgO	723	0.6	[14]
MoMgO	773	5.5	[14]
MgVO	773	2.8	[15]
$Mg_3V_2O_8$	823	0.4	[15]
α-$Mg_2V_2O_7$	823	3.5	[16]
α-MgV_2O_6	823	1.0	[16]
Mo–Mg/Al_2O_3	723	1.8	[9]
Mo–Mg–O	723	1.6	[8]
$MgMoO_4$	823	1.1	[6]
Our catalyst	623	1.5	
Our catalyst	673	6.4	

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support and mixed with spatula. The impregnated samples were dried at 373 K and then calcined at 873 K for 5 h. The x values were 3, 5, 10 and 20 wt%.

Catalysts with different Mo/Mn atomic ratios were also prepared by a citrate method (Mo/Mn catalysts). Manganese carbonate and citric acid were dissolved in distilled water, and then $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was added to the solution. After evaporation of the solvent in a rotating vessel at about 323 K under reduced pressure, the solid obtained was dried at 373 K overnight. After calcination at 773 K for 24 h, Mo/Mn 1 : 1; Mo/Mn 1.15 : 1 and Mo/Mn 1.5 : 1 catalysts were obtained.

The catalysts (0.5–0.85 mm particles diameter) were tested in a fixed-bed, quartz tubular reactor operated at atmospheric pressure over a wide range of temperatures (523–823 K). The temperature was measured with a coaxial thermocouple. The feed was a mixture of 4 vol% propane, 4 vol% oxygen and the balance helium. The flow rate was 100 ml/min at room temperature. The reactants and reaction products were alternately analyzed on-line by a Shimadzu GC9A gas chromatograph equipped with a thermal conductivity detector. A Porapak Q (80–100 mesh) column for separating hydrocarbons and CO_2 and a 2 m activated carbon (30–50 mesh) column for carbon monoxide, methane and oxygen were used. The catalyst weight was 1 g.

Specific surface areas (S_{BET}, m^2/g) of all samples were determined from nitrogen adsorption isotherms at 77 K by the BET method. A Micromeritics Accusorb 2100E was used. X-ray diffraction (XRD) patterns were obtained by using a Rigaku diffractometer operated at 30 kV and 20 mA by employing Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm).

3. Results and discussion

Table 2 summarizes the physical properties of the catalysts. The specific surface decreased by approximately 30% after impregnation, independently of the molybdenum loading. X-ray diffractograms did not exhibit MoO_3 patterns in any case, while those corresponding to $MnMoO_4$ were detected for molybdenum loading of 5%, with increased intensity for 10% loading. The predominant phase of the manganese oxide support was Mn_2O_3.

It is evident that the system defined from the impregnated catalysts evolves by means of a reaction in the solid state to the formation of the $MnMoO_4$ phase. The catalyst preparation includes conditions that favour this solid state reaction. Cadus et al. [6], have shown that in analogous

Table 2
BET specific surface and X-ray diffraction for both impregnated and Mo/Mn catalysts.

Catalyst	S_{BET} (m^2/g)	XRD phases
Mn_2O_3	15.0	Mn_2O_3 (10-69)
i3Mo/Mn_2O_3	11.3	Mn_2O_3 (10-69)
i5Mo/Mn_2O_3	10.8	$Mn_2O_3 + MnMoO_4$ (27-1280)
i10Mo/Mn_2O_3	10.2	$Mn_2O_3 + MnMoO_4$ (27-1280)
Mo/Mn 1 : 1	1.88	MoO_3 (5-508) + $MnMoO_4$ (27-1280)
Mo/Mn 1.15 : 1	0.94	MoO_3 (5-508) + $MnMoO_4$ (27-1280)
Mo/Mn 1.50 : 1	0.90	MoO_3 (5-508) + $MnMoO_4$ (27-1280)

Table 3
Catalytic activity of ixMo/Mn_2O_3 and Mo/Mn catalysts.

Catalyst	T_R (°C)	C_3H_8 conv. (%)	Selectivity (%)					C_3H_6 yield (%)	STY C_3H_6 (g/kg h)
			C_3H_6	C_2H_4	CH_4	CO	CO_2		
Mn_2O_3	573	20.14	2.86				97.14	0.57	
i3Mo/Mn_2O_3	623	1.23	82.93	–	–	–	17.07	1.02	4.6
i3Mo/Mn_2O_3	673	1.92	63.92	–	–	–	36.08	1.23	5.5
i3Mo/Mn_2O_3	723	5.26	58.01	–	–	–	41.99	3.05	13.7
i3Mo/Mn_2O_3	773	16.06	40.22	–	–	15.33	44.45	6.46	29.1
i3Mo/Mn_2O_3	823	30.76	29.33	1.47	–	10.69	58.51	9.02	40.6
i5Mo/Mn_2O_3	623	1.57	80.25	–	–	–	19.75	1.26	5.67
i5Mo/Mn_2O_3	673	2.13	65.09	–	–	–	34.91	1.38	6.21
i5Mo/Mn_2O_3	723	5.44	58.81	–	–	–	41.19	3.20	14.4
i5Mo/Mn_2O_3	773	16.46	38.7	–	–	16.19	45.11	6.37	28.67
i5Mo/Mn_2O_3	823	30.37	29.79	1.31	–	12.91	55.98	9.02	40.59
i10Mo/Mn_2O_3	623	1.98	76.26	–	–	–	23.74	1.51	6.8
i10Mo/Mn_2O_3	673	3.17	53.21	–	–	–	46.79	1.69	7.6
i10Mo/Mn_2O_3	723	8.02	48.19	–	–	–	51.81	3.86	17.4
i10Mo/Mn_2O_3	773	21.84	31.84	–	–	22.02	46.14	6.95	31.3
i10Mo/Mn_2O_3	823	29.78	29.20	1.41	–	6.38	63.01	8.69	39.1
MoMn 1 : 1	773	0.14		–	–	–			
Mo/Mn 1 : 1	823	2.25	93.45	–	–	–	6.55	2.10	9.45
Mo/Mn 1.15 : 1	773	0.72		–	–	–			
Mo/Mn 1.15 : 1	823	1.60	93.05	–	–	–	6.95	1.49	6.71
Mo/Mn 1.5 : 1	673	0.19		–	–	–			
Mo/Mn 1.5 : 1	723	0.36		–	–	–			
Mo/Mn 1.5 : 1	773	1.06		–	–	–			
Mo/Mn 1.5 : 1	823	1.91	90.85	–	–	–	9.15	1.74	7.83

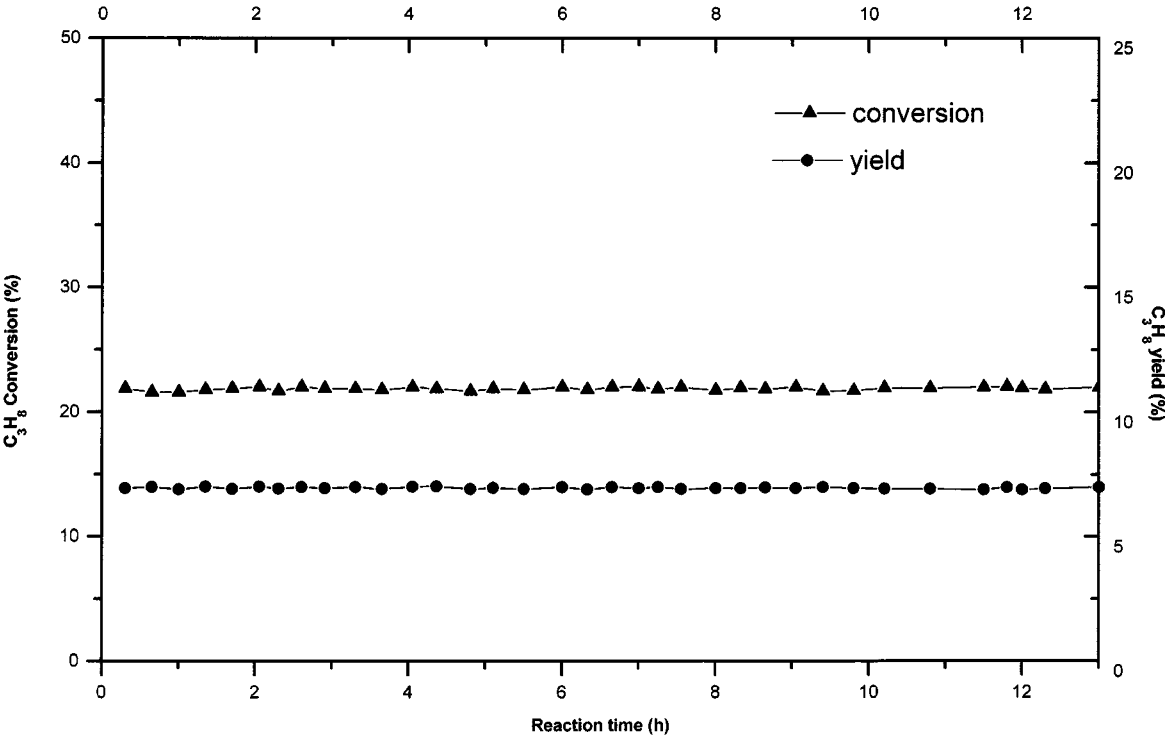

Figure 1. Stability test of the i10Mo/Mn_2O_3 catalyst at 773 K.

systems consisting of a Mo base catalyst, the Mo^{6+}–Mo^{5+} coupled pair plays a major role in catalytic activity. It has been observed that during and after the catalytic reaction the system tends to achieve balance as a reduced system, in which the adsorbed and reacting species are critical for the redefinition of surface architecture.

The catalytic activity data of the different catalysts in terms of C_3H_8 conversion, product distribution, yield to C_3H_6 and C_3H_6 productivity values, are presented in table 3. Appropriate blank runs showed that, under our experimental conditions, the contribution of the gas phase reaction up to 873 K is negligible.

The results summarized in table 3 indicate that this type of catalysts, unlike the ones usually reported in the literature exhibit a very high CO_2/CO ratio. Apparently, Mn_2O_3 promotes the oxidation of non-desorbed olefin species. The ability of manganese oxides to catalyze the reaction of hydrocarbides to total oxidation products is well known. The activation of propane and its oxidehydrogenation to propene at temperatures as low as 623 K, with a yield to C_3H_6 of approximately 1.5%, is remarkable (see table 1). This temperature is 100 K lower than that reported by other authors for the most commonly used systems. It has even been found that on manganese oxide with its principal crystalline phase identified as Mn_3O_4, the activation of propane to propene becomes evident only at 723 K [11].

The performance of the i10Mo/Mn_2O_3 catalyst at 773 K in terms of C_3H_8 conversion and yield of C_3H_6 as a function of time on stream is presented in figure 1. The obtained data, under the conditions described in section 2, show that this catalyst is very stable in propane ODH. The catalytic results shown by those catalysts whose principal phases are $MnMoO_4$ and MoO_3 (Mo/Mn 1 : 1, 1.15 : 1 and 1.5 : 1) indicate that the surface array of impregnated catalysts determines the activation of C_3H_8 to C_3H_6 at low temperatures.

Taking into consideration their ability to give high propene yields as well as considerable productivity values, Mo–Mn–O catalysts can be considered to have a potential for the reaction under study.

In conclusion, Mo–Mn–O catalysts prepared from dry impregnation of Mo on Mn_2O_3 were found to catalyze the oxidehydrogenation of propane to propene at 623 K. Additional investigations are in progress, devoted to highlighting the nature of the active sites of the ixMo/Mn_2O_3 catalysts in the oxidehydrogenation of propane as well as the factors controlling the final surface architecture.

Acknowledgement

Financial support is acknowledged to CONICET and to Universidad Nacional de San Luis.

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