V–Mg–O prepared via a mesoporous pathway: a low-temperature catalyst for the oxidative dehydrogenation of propane to propene

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Received 14 January 2004; accepted 3 March 2004

The oxidative dehydrogenation of propane was investigated in a fixed-bed tubular flow reactor at 350 and 450 °C over V–Mg–O catalysts prepared via a solid reaction (the mix-VMg catalysts) or from mesoporous precursors (the meso-VMg catalysts). Significantly higher selectivities and yields to propene were obtained over the meso-VMg catalysts than over the mix-VMg ones. The cooperation between a much higher BET specific surface area and a novel phase, a highly dispersed-Mg-in-V_2O_3, is suggested as responsible for the higher ODP performance of the meso-VMg catalysts than of the mix-VMg ones.

KEY WORDS: mesoporous; vanadium; magnesium; catalyst; oxidative dehydrogenation; propane; propene.

1. Introduction

The oxidative dehydrogenation of propane (ODP) to propene has received extensive attention, because of the increased demand for propene. Compared to the commercial production of propene via non-oxidative dehydrogenation [1–3], the ODP process is potentially advantageous, because the reaction is exothermic and employs a cheaper and more abundant raw material. The ODP reaction has a relatively low selectivity, because propene is more reactive than propane and is prone to side reactions, such as cracking and combustion. At moderate temperatures, these processes are mainly heterogeneous and could be controlled by the appropriate choice of a catalyst. The development of such a catalyst with a sufficiently high activity and selectivity at low temperatures is thus highly desirable. Many catalysts have been reported for the ODP reaction and the V–Mg–O system appears to be among the most promising ones [4–23]. Most of the results obtained with the latter catalysts were at temperatures higher than 500 °C, and only few were concerned with 500 °C or lower temperatures [21–23]. Very small conversions and yields were obtained at low temperatures. The present paper deals with the ODP reaction at 350 and 450 °C over V–Mg–O catalysts of various V/Mg atomic ratios, prepared via a solid reaction (mix-VMg) or from mesoporous precursors (meso-VMg). The results have clearly demonstrated that the catalysts based on mesoporous V–Mg–O are more active and selective than those prepared through a solid reaction. The yields provided by the latter catalysts (mix-VMg) are comparable to those reached previously [21–23].

2. Experimental

Two groups of catalysts, namely mix-VMg and meso-VMg, were prepared and the information regarding their preparation and characterization is summarized in tables 1 and 2. The mix VMg catalysts were prepared via a solid reaction between V_2O_5 and $MgCl_2$ by mixing their powders and heating in air at 750 °C for 2 h after they were heated at a rate of 4 °C/min from room temperature. The mesoporous V–Mg–O were synthesized at room temperature by dispersing vanadium acetylacetonate ($V(acac)_3$) into distilled water, and dissolving $MgCl_2$ and the template (cetyltrimethylammonium bromide (CTAB) or an equimolar mixture of CTAB and sodium dodecylbenzene sulfonate (SDBS)) into a HCl aqueous solution, and then mixing the two systems. The mixture was continuously stirred for 24 h and then allowed to age statically for 2 days. The pH was adjusted to 10 during aging. A mesoporous vanadium oxide was also prepared from V_2O_5 and an equimolar mixture of CTAB and hexadecylamine (HDA) using a similar procedure, except that V_2O_5 was dissolved into a NaOH aqueous solution, and the pH was adjusted to 7 during aging. The solid specimens were recovered by filtering, washing and drying and used for characterization and preparation of the catalysts. The meso-VMg catalysts were prepared by calcining the mesoporous V–Mg–O precursors in a flow of argon at 750 °C for 4 h after they were heated at a rate of 10 °C/min from room temperature.

The phases present in the specimens were identified by X-ray diffraction (XRD) on a SIEMENS D500 diffractometer with a CuK_α radiation of 1.5406 Å. The diffraction data were recorded for 2θ angles ranging between 1 and 50°, with a resolution of 0.02°. The textural properties of the catalysts were determined by N_2 adsorption using a Micromeritics ASAP 2010 Gas

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Table 1
Preparation conditions, phases and properties of the mesoporous V–Mg oxides and the corresponding meso-VMg catalysts

Catalysts	Mole composition in initial batch	V/Mg atomic ratio		S_{BET}[a] (m^2/g)	PV[b] (cm^3/g)	APS[c] (nm)	Phases identified by XRD	
		AAS	XPS				As-synthesized	Calcination at 750 °C
meso-VMg-1	$1.6V(acac)_3 : 0.4MgCl_2 : 0.25CTAB : 295H_2O$	48.23	6.82	151.0	0.17	4.51	Hexagonal	V_2O_3
meso-VMg-2	$1.2V(acac)_3 : 0.8MgCl_2 : 0.25CTAB : 295H_2O$	35.29	0.82	155.1	0.18	4.66	Hexagonal	V_2O_3
meso-VMg-3	$0.6V(acac)_3 : 1.2MgCl_2 : 0.25CTAB : 295H_2O$	10.65	7.06	159.1	0.16	4.05	Hexagonal	V_2O_3
meso-VMg-4	$0.4V(acac)_3 : 1.6MgCl_2 : 0.25CTAB : 295H_2O$	1.39	2.09	159.8	0.19	4.77	Hexagonal	V_2O_3, $Mg_{1.5}VO_4$, MgO
meso-VMg-5	$V(acac)_3 : MgCl_2 : (0.125CTAB+0.125SDBS) : 295H_2O$	3.19	5.12	158.5	0.16	3.99	Hexagonal	V_2O_3, $Mg_{1.5}VO_4$, MgO
meso-V	$V_2O_5 : (0.125CTAB+0.125HDA) : 295H_2O$	–	–	148.6	0.28	7.56	Lamellar	V_2O_3

[a] S_{BET}: BET specific surface area.
[b] PV: pore volume.
[c] APS: average pore size.

Sorption and Porosimetry instrument. The specific surface area was determined by the BET method, the pore volume was calculated at a relative pressure of $P/P_0 > 0.99$, and the pore size distribution was calculated by the BJH method. The bulk V/Mg atomic ratios of the catalysts were determined by Atomic Absorption Spectrophotometry (AAS) using a Perkin-Elmer model AAS 3030 spectrophotometer. The surface V/Mg atomic ratios were determined by X-ray photoelectron spectroscopy (XPS) with a VG-ESCA lab-210 spectrometer, using MgK_α radiation as the excitation source.

The results of the characterization are listed in table 1 for the meso-VMg catalysts and in table 2 for the mix-VMg catalysts.

The catalytic tests for the ODP reaction were carried out at atmospheric pressure in a fixed-bed quartz tubular flow reactor (internal diameter = 5 mm and operation length = 30 cm). A small amount (0.2 g) of catalyst was loaded in the middle of the reactor, and above the catalyst bed quartz granules were introduced to quench the possible homogeneous reactions. A feed mixture with a mole composition of 90% propane, 4% oxygen and 6% nitrogen was continuously passed through the reactor, which was heated at 350 or 450 °C. The compositions of the feed and the product mixtures were analyzed on-line using a SRI 8610C gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). A Hayesep DB ($30' \times 1/8''$) packed column was employed to separate the mixtures.

3. Results and discussion

The ODP reactivities at 350 and 450 °C over V_2O_5, MgO and the mix-VMg catalysts are listed in table 3. No conversions in an empty reactor and in a reactor filled with quartz granules were detected. Consequently, any conversion of propane in the presence of a catalyst was the result of the catalytic process. The pure V_2O_5 exhibited a somewhat higher ODP performance than the pure MgO, with a higher selectivity to propene and a slightly higher conversion of propane. Compared to the pure V_2O_5, the mix-VMg catalysts provided much higher conversions of propane, but lower selectivities to propene. For all mix-VMg catalysts, the elevation of the reaction temperature from 350 to 450 °C increased both the conversion of propane and the selectivity to propene, and the increase of the flow rate improved the selectivity to propene but reduced the conversion of propane. With the decrease of V/Mg atomic ratios in the mix-VMg catalysts, the conversion of propane increased but the selectivity to propene passed through a maximum. The highest selectivity to propene was provided by the mix-VMg-3 catalyst. The mix-VMg catalysts provided yields comparable to those obtained previously with similar V–Mg–O catalysts [21–23].

Table 2
Properties of mix-VMg catalysts and the phases they contained

Catalyst	V/Mg atomic ratio	S_{BET}[a] (m^2/g)	PV[b] (cm^3/g)	APS[c] (nm)	Phase identified by XRD[d]
V_2O_5	∞	4.75	0.010	8.28	V_2O_5
mix-VMg-1	4.0	1.02	0.0028	10.83	V_2O_5 and *m*
mix-VMg-2	2.0	2.19	0.0071	12.65	V_2O_5 and *m*
mix-VMg-3	1.0	3.36	0.0017	10.63	MgO, *m* and *p*
mix-VMg-4	0.5	6.54	0.0017	10.61	MgO, *m* and *p*
mix-VMg-5	0.25	7.16	0.023	12.78	MgO, *m*, *p* and *o*
MgO	0	14.10	0.043	12.20	MgO

[a–c] See table 1.

[d] *m*, *p* and *o* refer to *m*-MgV_2O_6, *p*-$Mg_2V_2O_7$, *o*-$Mg_3(VO_4)_2$, respectively.

Table 3
ODP reactivities over mix-VMg catalysts

Catalysts	*F*[a] (mL/s)	*X*[b] (%)	Selectivity (%)						*Y*[c] (%)
			CO_x	CH_4	C_2H_4	C_2H_6	C_3H_6	C_{4+}	
350 °C									
V_2O_5	5.63	0.05	0.00	0.00	0.00	54.63	45.37	0.00	0.02
	2.37	0.44	51.00	1.00	0.00	2.77	41.21	4.02	0.18
MgO	5.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
mix-VMg-1	2.37	3.81	81.77	0.00	0.19	6.96	5.43	5.65	0.21
mix-VMg-2	2.37	4.68	76.37	0.00	0.31	5.49	15.48	2.35	0.72
mix-VMg-3	2.37	4.80	73.90	0.00	0.56	5.42	18.55	1.57	0.89
mix-VMg-4	2.37	6.85	81.40	0.00	0.73	4.84	11.48	1.55	0.79
mix-VMg-5	2.37	7.03	86.88	0.00	0.98	3.61	6.99	1.54	0.49
mix-VMg-5	5.63	1.56	49.98	0.25	0.50	6.42	33.44	9.41	0.52
450 °C									0.00
V_2O_5	5.63	0.33	0.00	0.75	6.20	37.73	50.32	5.00	0.17
	2.37	2.01	53.88	0.29	0.71	2.21	39.52	3.39	0.79
MgO	5.63	0.06	14.01	1.78	14.28	28.91	35.44	5.58	0.02
	2.37	0.15	24.00	2.29	16.57	12.53	30.75	13.87	0.05
mix-VMg-1	2.37	4.88	77.19	0.00	0.31	5.21	12.51	4.78	0.61
mix-VMg-2	2.37	5.72	61.88	0.00	1.10	4.71	30.00	2.31	1.72
mix-VMg-3	2.37	6.58	49.33	0.00	1.50	3.73	43.89	1.55	2.89
mix-VMg-4	2.37	7.59	73.50	0.31	1.91	3.44	19.55	1.29	1.48
mix-VMg-5	2.37	8.34	76.74	0.57	2.31	2.34	17.31	0.73	1.44
mix-VMg-5	5.63	4.11	38	0.26	7.59	4.59	44.81	4.75	1.84

[a] *F*: flow rate.

[b] *X*: conversion of propane.

[c] *Y*: yield of propene.

The ODP reactivities at 350 and 450 °C over the meso-VMg catalysts are listed in table 4. It was found that the meso-V provided a higher conversion of propane but a lower selectivity to propene than V_2O_5. At the temperatures of 350 and 450 °C and a flow rate of 5.63 mL/s, propane conversions of 1.08% and 1.31% and propene selectivities of 7.62% and 14.46%, respectively, were attained over meso-V. However, over the meso-VMg catalysts, the ODP performance was significantly improved. At the temperatures of 350 and 450 °C, propane conversions of 7.73% and 9.96% and propene selectivities of 89.22% and 72.13%, respectively, were reached over the meso-VMg-5 catalyst. When the temperature was increased from 350 to 450 °C, the conversion of propane increased for all V/Mg bulk atomic ratios. However, the selectivity to propene increased with increasing temperature for the catalysts with bulk atomic ratios of V/Mg $>$ 10 (meso-VMg-1, meso-VMg-2 and meso-VMg-3), but decreased for the other catalysts (meso-VMg-4 and meso-VMg-5). With increasing V/Mg bulk atomic ratio, the conversion of propane decreased. High selectivities to propene were achieved for most V/Mg bulk ratios. The highest selectivities were obtained over the catalysts with smaller V/Mg surface ratios. The increase in the flow rate increased the selectivity to propene but reduced the propane conversion.

Comparing tables 3 and 4, one can conclude that the meso-VMg catalysts provided much higher ODP

Table 4
ODP reactivities over meso-VMg catalysts

Catalysts	F^a (mL/s)	X^b (%)	Selectivity (%)						Y^c (%)
			CO_x	CH_4	C_2H_4	C_2H_6	C_3H_6	C_{4+}	
350 °C									
meso-V	5.63	1.08	88.06	0.03	0.07	2.32	7.62	1.89	0.08
meso-V	2.37	2.55	88.67	0.05	0.10	3.58	5.49	2.11	0.14
meso-VMg-1	2.37	3.87	79.13	0.05	0.25	1.01	19.36	0.20	0.75
meso-VMg-2	2.37	8.48	0	0	2.12	17.78	75.07	5.03	6.36
meso-VMg-3	2.37	7.37	0	0	1.66	30.49	55.96	11.89	4.12
meso-VMg-4	2.37	7.84	0	0	1.67	20.06	72.83	5.44	5.71
meso-VMg-5	2.37	8.11	0	0	0	35.03	51.61	13.36	4.19
meso-VMg-5	5.63	7.73	0	0	0	5.85	89.22	4.94	6.90
450 °C									
meso-V	5.63	1.31	83.68	0.06	0.36	0.69	14.46	0.76	0.19
meso-V	2.37	7.08	86.94	0.13	0.41	1.36	10.87	0.29	0.77
meso-VMg-1	2.37	8.61	69.15	0.10	0.38	0.82	29.37	0.18	2.53
meso-VMg-2	2.37	10.60	15.10	0.10	0.96	2.33	80.75	0.75	8.56
meso-VMg-3	2.37	11.50	0	0	2.83	15.49	80.61	1.06	9.27
meso-VMg-4	2.37	11.13	41.28	0	0.80	1.69	55.84	0.39	6.21
meso-VMg-5	2.37	10.75	0	0.68	1.51	34.82	45.84	17.15	4.93
meso-VMg-5	5.63	9.96	22.04	0	0.43	2.12	72.13	3.28	7.18

[a] F: flow rate.
[b] X: conversion of propane.
[c] Y: yield of propene.

performances, particularly for the selectivity to propene, than the mix-VMg catalysts. The difference between the reactivities of the meso-VMg and mix-VMg catalysts is probably caused by their different phase structures and textural properties. As one can see from tables 1 and 2, all the meso-VMg catalysts possessed much larger specific surface areas and pore volumes than the mix-VMg catalysts. However, this does not mean that the higher performance of the meso-VMg catalysts is solely caused by the increased specific surface area and pore volumes. In fact, as already noted, the meso-V catalyst (BET area = 148.6 m^2/g and pore volume = 0.28 cm^3/g) did not perform better than any of the mix-VMg catalysts (BET area ≤ 7.16 m^2/g and pore volume ≤ 0.023 cm^3/g). This hints that the phase structure of the catalyst constitutes an equally important factor that affects the ODP performance. From table 2, one can see that depending on the V/Mg atomic ratio, the mix-VMg catalysts contained either a V_2O_5 or a MgO phase together with one or more magnesium vanadate phases. In the meso-VMg catalysts, only the V_2O_3 phase could be identified by XRD for bulk atomic ratios of V/Mg > 10, and V_2O_3 and MgO together with an additional magnesium vanadate, $Mg_{1.5}VO_4$, for the catalysts with V/Mg < 10. The fact that none of Mg-containing phases could be detected by XRD for bulk atomic ratios of V/Mg > 10 may mean that magnesium was highly dispersed into or onto the V_2O_3 phase. XPS investigations have provided proof in this direction. As shown in table 1, the surface atomic ratios of V/Mg were smaller for the meso-VMg-1, meso-VMg-2 and meso-VMg-3 (for which the bulk atomic ratios of V/Mg > 10), but larger for the meso-VMg-4 and meso-VMg-5 (for which the bulk atomic ratios of V/Mg < 10) than the corresponding bulk atomic ratios. This indicates that there is an enrichment in Mg on the surface of the meso-VMg catalysts for bulk atomic ratios of V/Mg > 10, but not for the meso-VMg catalysts with bulk atomic ratios of V/Mg < 10. Thus, Mg must be highly dispersed onto the V_2O_3 phase in the former meso-VMg catalysts; otherwise, the Mg-containing phases would have been detected by XRD in the meso-VMg catalysts with bulk atomic ratios of V/Mg > 10. Consequently, the high specific surface area associated with the meso-VMg catalysts may provide a medium in which Mg species could become highly dispersed onto the V_2O_3 phase. In this manner, an active phase, which can provide active sites, for example, some active lattice oxygen species or active vanadium centers, may be formed. In addition, the high pore volume of the meso-VMg catalysts can facilitate the diffusion and thus improve the selectivity of the ODP reaction. These conclusions are similar to those reached by us regarding the oxidative dehydrogenation of ethane [24,25]. Consequently, it is expected the meso-VMg catalysts to be high-performance ODP catalysts.

4. Conclusion

The Meso-VMg catalysts, prepared by calcining mesoporous V–Mg–O precursors, were more selective and active for the ODP reaction at the low temperatures of 350 and 450 °C employed in the present paper than the mix-VMg ones, prepared via a solid reaction between vanadia and magnesia. The high specific surface areas of the meso-VMg catalysts provided a medium in which Mg species could be highly dispersed over or into the V_2O_3 phase. The highly dispersed-Mg-in-V_2O_3 might have generated active sites, such as some lattice oxygen species or vanadium centers that enhanced the ODP reaction. In addition, the high porosity promoted the diffusion of the species involved in the reaction. These characteristics of the meso-VMg catalysts make them promising candidates as high-performance ODP catalysts.

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