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Effect of Coexistence of Magnesium Vanadate Phases in the Selective Oxidation of Propane to Propene

Xingtao Gao,* P. Ruiz,† Qin Xin,* Xiexian Guo,* and B. Delmon†

**State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China; and †Universite Catholique de Louvain, Unité de Catalyse et Chimie des Matériaux Divises, Place Criox du Sud 2 boite 17, 1348 Louvain-la-Neuve, Belgium*

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The study of oxidative dehydrogenation of propane was carried out over V–Mg–O catalysts. The citrate method was used to prepare catalysts with the Mg/V atomic ratio varying from 1/4 to 9/1. Three pure Mg vanadates and the corresponding biphasic catalysts were obtained from very homogeneous Mg–V–citrate precursors after calcination at 550°C. Among the three pure Mg vanadates, α-$Mg_2V_2O_7$ (pyrovanadate) was found to be the most selective, while MgV_2O_6 (metavanadate) is the worst one. Interestingly, the catalytic behavior of biphasic catalysts is quite different from that of pure Mg vanadate phases. For example, the selectivity of $Mg_3V_2O_8$ (orthovanadate) can be promoted by a coexisting pyrovanadate phase or excess magnesium oxide in intimate contact. These differences are discussed in terms of the different specific activities of phases and possible synergy effects between the phases. © 1994 Academic Press, Inc.

INTRODUCTION

The transformation of alkanes into useful intermediates is currently the object of intense investigations in the field of catalysis. The oxidation of butane to maleic anhydride constitutes an outstanding but quite exceptional success in the area of catalysis. Most reactions of light alkanes are still fairly selective. Transformation of ethane and especially propane to the corresponding olefins by reaction with oxygen is, in principle, a very attractive alternative to steam cracking.

The present work deals with V–Mg–O catalysts, which are active and relatively selective in the oxidative dehydrogenation of propane and butane (1, 2). Three Mg vanadate phases were found to form in V–Mg–O catalysts as a function of vanadium concentration and calcination temperature (3). Kung and co-workers attributed the active phase primarily to Mg orthovanadate (1, 2). In propane oxidation, they observed similar selectivity for Mg pyrovanadate and orthovanadate phases (4). However, Volta and co-workers (3) suggested that Mg pyrovanadate was the active phase, and orthovanadate was responsible for total oxidation.

Previous studies have focused on the specific Mg vanadate phases. Although two isolated phases have been proposed to be responsible for the selective oxidation of propane, it must be noted from those studies (2, 3) that in their V–Mg–O working catalysts, at least two phases have been identified simultaneously. Thus, it is reasonable to suspect that the overall catalytic behavior should not be attributed to just one phase. In this aspect, it becomes interesting to investigate whether the coexistence of phases plays a role in the selective oxidation of propane over V–Mg–O catalysts. We report here the results of this investigation.

The present work will focus on the physicochemical characterization of catalysts, comparison of catalytic properties between pure Mg vanadate phases and multiphase catalysts, and investigation of the interaction between phases.

EXPERIMENTAL

Catalyst Preparation

(*a*) *Preparation of V–Mg–O catalysts.* Samples with Mg/V atomic ratios varying from 1/4 to 9/1 were prepared by the citrate method (5). In what follows, samples will be identified by the corresponding Mg/V atomic ratio in parentheses. The starting materials used were Mg $(NO_3)_2 \cdot 6H_2O$ and NH_4VO_3 (p.a.; ucb). This method provides the following advantages: (a) the expected oxide compounds can be obtained from very homogeneous citrate precursors, (b) lower calcination temperature can be used (550°C), and (c) no contamination from other residual elements is observed.

The detailed preparation procedure applied to V–Mg–O catalysts has been described elsewhere (6). Briefly, a transparent solution of magnesium nitrate and ammonium metavanadate with a Mg/V atomic ratio equal to that of the resulting catalyst was prepared, followed by the addition of citric acid. Subsequently, the citrate solution was evaporated in a Rotavapor to obtain amorphous organic

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precurser. The resulting solid was then decomposed at 380°C for 18 h and finally calcined at 550°C for 6 h.

The same pocedure was also used to prepare pure MgO and V_2O_5 in order to permit a comparison with the V–Mg–O catalysts.

(*b*) *Preparation of mechanical mixtures.* Mechanical mixtures of (1/1)MgVO + (3/2)MgVO and (3/2)MgVO + MgO denoted MPO and MOM, respectively, have been made. Identical weights (1 : 1) of the corresponding powders were dispersed and mixed in *n*-pentane with the help of a supersonic device, and were subsequently evaporated under reduced pressure to remove the solvent. The solid obtained was then dried at 80°C overnight. The mixtures were used without further treatment.

Catalyst Characterization

The BET surface areas were determined by Krypton ($S_{BET} < 20$ m^2/g) or nitrogen adsorption ($S_{BET} > 20$ m2/g) in an automatic ASAP 2000 equipment constructed by Micromeritics. The actual compositions were determind by atomic absorption spectroscopy after the catalysts were dissolved in 0.1 *M* nitric acid.

X-ray diffraction was performed on a Siemens Diffrac-500 using Cu*Kα* radiation. JCPDS-ICDD (1990–1991) standard spectra software was employed to determine the phases.

Infrared spectra were recorded between 1200 and 350 cm^{-1} with a Bruker IFS 88B. The sample was mixed with KBr (2/300 by weight) and pressed into a thin wafer.

Raman spectra were collected with a Jovin Ivon Ramanor U-100 double monochromatic spectrometer. The samples were pressed into self-supporting 15 mm-diameter wafers and mounted on a rotating plate. The spectra were collected using the 514.5-nm line as exciting radiation for a Spectra-Physics series 2000 Ar ion laser. The laser power used was 200 mW (measured at the source).

The XPS spectra were taken with an SSX-100 Model 206 ESCA spectrometer. The exciting radiation was Al*Kα* (1486.6 eV). The spot size was 1000 μm. The flood gun was used at 6.0 eV. Atomic concentration ratios were calculated by correcting the intensity ratios with theoretical sensitivity factors proposed by the manufacturer, i.e., 0.64 for Mg_{2S}, 8.33 for V_{2P}, and 2.49 for O_{1S}. B.E. were calculated with respect to C_{1S} (284.8 eV). Two fitting constraints were used to aid the fitting of V_{2P}: the area ratio between $V_{2P_{3/2}}$ and $V_{2P_{1/2}}$ is equal to 1.94, the difference of B.E. between $V_{2P_{1/2}}$, and $V_{2P_{3/2}}$ is 7.5 eV.

Catalyst Test

The catalyst test was performed in a flow system. The sample with particle fractions between 500 and 800 μm was placed on a fixed bed (inner diameter 15 mm) in a U-type quartz microreactor. Under standard conditions, the feed was 4 vol% propane (UCAR, IP), 8% oxygen, and the balance He. The total flow rate was 50 ml/min, and the reaction temperature was 450 to 540°C. Normally, a 0.3-g sample was used. The empty reactor showed no activity. Although the surface areas of some catalysts after reaction decreased a little (within 10%), no noticeable deviation was observed during the test.

The reaction products were analyzed by a Shimadzu C-R6A on-line gas chromatograph. Helium was the carrier gas. Two columns were used in parallel: a VZ-7 (60/80 mesh, Alltech Associates, Inc.) column at 40°C to separate the hydrocarbons and CO_2, and a molecular sieve 5A column to separate O_2 and CO. The conversion of propane, *C* (%), is defined as the percentage of propane feed which has reacted. Conversion per catalyst surface area, *C* m^{-2}, was also calculated. This roughly reflects the intrinsic activity of the catalysts. The yield of propene, *Y* (%), is the percentage of propane feed which has reacted to propene. The selectivities are defined as the percentage of propane which reacts to a specific product.

RESULTS

Catalyst Characterization

BET measurement. The surface areas and the actual compositions are listed in Table 1. Except for some fluctuations, the surface areas increase as the Mg/V atomic ratio increases. The maximum value was obtained with the (9/1)MgVO catalyst. The actual bulk (Mg/V) atomic ratios are very near the theoretical values, because the catalysts have obtained by evaporation of the solvent with no loss of chemical compounds during the preparation. The color of the catalysts varies from orange to white, followed by light yellow at higher Mg/V ratios (4/1, 9/1).

TABLE 1

Compositions and Surface Areas of Catalysts

Catalysts	Surface area (m^2/g)	Colour	Composition		
			MgO (mol%)	V_2O_5 (mol%)	Mg/V
V_2O_5	2.3	orange	0	100	
(1/4)MgVO	3.4	orange	35.5	64.5	0.28
(1/2)MgVO	2.7	yellow	51.1	48.9	0.52
(3/4)MgVO	8.1	yellow	60.9	39.1	0.78
(1/1)MgVO	8.3	milk white	67.4	32.5	1.04
(5/4)MgVO	13.8	milk white	72.5	27.5	1.32
(3/2)MgVO	22.8	white	75.7	24.3	1.56
(7/4)MgVO	35.5	white	77.8	22.2	1.75
(4/1)MgVO	55.0	light yellow	89.3	10.7	4.17
(9/1)MgVO	127.7	light yellow	94.9	5.1	9.30
MgO	75.8	white	100	0	

TABLE 2

Identification of V–Mg–O Catalysts by X-Ray Diffraction

Catalysts	Phases Identified
(1/4)MgVO	V_2O_5 + MgV_2O_6
(1/2)MgVO	MgV_2O_6
(3/4)MgVO	MgV_2O_6 + $\alpha Mg_2V_2O_7$
(1/1)MgVO	$\alpha Mg_2V_2O_7$
(5/4)MgVO	$\alpha Mg_2V_2O_7$ + $Mg_3V_2O_8$
(3/2)MgVO	$Mg_3V_2O_8$
(7/4)MgVO	$Mg_3V_2O_8$
(4/1)MgVO	MgO + $Mg_3V_2O_8$
(9/1)MgVO	MgO + $Mg_3V_2O_8$

X-ray diffraction. The characterization results of V–Mg–O catalysts by XRD analysis are shown in Table 2. As expected, the phases identified correspond to their Mg/V atomic ratios. Five pure phases, V_2O_5, MgV_2O_6, α-$Mg_2V_2O_7$, $Mg_3V_2O_8$, and MgO, and mixtures of phases corresponding to those in neighboring phases in the sequence are obtained (7–10).

Figure 1 illustrates the XRD spectra of (1/2)MgVO, (1/1)MgVO, and (3/2)MgVO. They are in good agreement with the standard spectra of MgV_2O_6, α-$Mg_2V_2O_7$, and $Mg_3V_2O_8$, respectively (8–10). Very small phase impurities in α-$Mg_2V_2O_7$, and $Mg_3V_2O_8$ are detected, and remain after catalytic reactions.

Figures 2 and 3 show the XRD spectra of the mixed phases. At (1/4), (3/4), and (5/4) each spectrum was constituted with the strong reflection lines of two phases. However, for (7/4)MgVO catalyst in Fig. 3a, the principal spectral feature corresponds almost exclusively to the contribution of the Mg orthovanadate phase. Compared to the pure $Mg_3V_2O_8$ phase, (7/4)MgVO should have some excess Mg oxide in addition to the orthovanadate phase (the theoretical phase ratio MgO: $Mg_3V_2O_8$ = 1 : 2). The small and large XRD rays associated with the small MgO particles present in the sample, which are not resolved from the very close $Mg_3V_2O_8$ rays, probably explain why no MgO phase was present in this sample. It should also be noted that the rays of the Mg orthovanadate phase are very poorly resolved and the peaks are very broad, thus making the resolution of the peak of MgO more difficult. The poor resolution and broadened peaks observed for (7/4)MgVO suggest also that the structure of Mg orthovanadate may be distorted and their particle sizes are very small.

When the Mg content is raised (Mg/V = 4/1, 9/1), the strong reflection lines of the MgO phase appear (Figs. 3b, 3c). However, broad peaks due to Mg orthovanadate can still be detected.

FT-IR study. Figure 4 shows the infrared spectra of (1/2)MgVO, (1/1)MgVO, and (3/2)MgVO. They are ascribed to MgV_2O_6, α-$Mg_2V_2O_7$, and $Mg_3V_2O_8$, respectively (6).

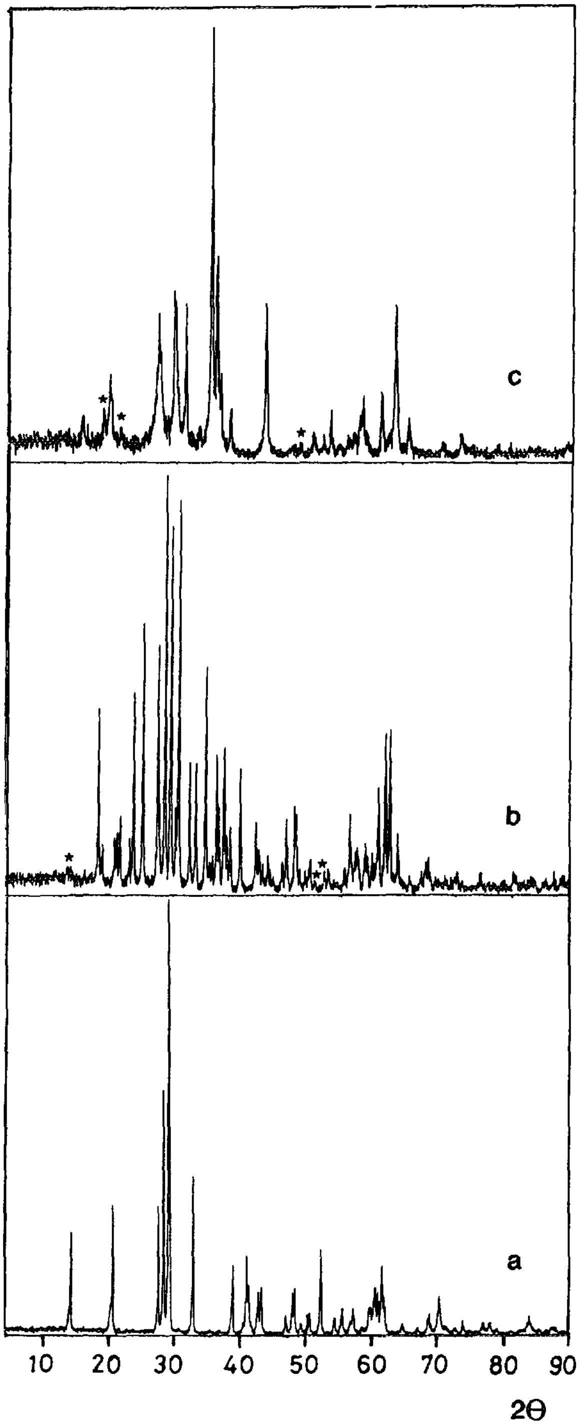

FIG. 1. X-ray diagrams of (a) (1/2)MgVO (MgV_2O_6), (b) (1/1)MgVO ($\alpha Mg_2V_2O_7$), (c) (3/2)MgVO ($Mg_3V_2O_8$). (★) impurities.

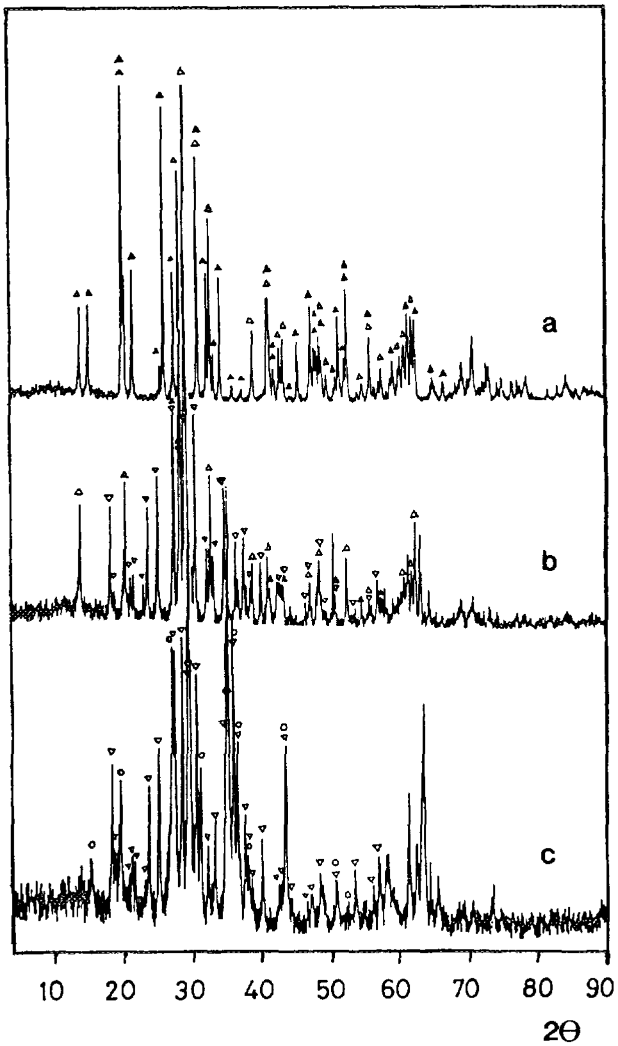

FIG. 2. X-ray diagrams of (a) (1/4)MgVO, (b) (3/4)MgVO, (c) (5/4)MgVO. (▲) V_2O_5, (△) MgV_2O_6, (▽) $\alpha Mg_2V_2O_7$, (○) $Mg_3V_2O_8$.

The infrared spectra of the biphasic catalysts are shown in Fig. 5. The (1/4)MgVO catalyst exhibits bands at 1020, 842, 633, 517, and 484 cm^{-1} due to the V_2O_5 oxide, and bands at 885, 678, 557, and 435 cm^{-1} due to the Mg metavanadate phase. The (3/4)MgVO catalyst possesses bands at 884 and 557 cm^{-1} due to Mg metavanadate, and strong bands at 976, 968, 920, 849, 824, 690, 672, 576, 458, 441, and 405 cm^{-1} due to the Mg pyrovanadate phase. In addition to the bands of Mg pyrovanadate, the (5/4)MgVO catalyst also displays bands at 862, 726, and 482 cm^{-1} due to the Mg orthovanadate phase. The (7/4)MgVO catalyst exhibits bands only due to Mg orthovanadate. For (4/1)MgVO, the broad bands at $\sim$849 and $\sim$695 cm^{-1} are most likely attributable to the Mg orthovanadate phase; however, a broad band at $\sim$493 cm^{-1} is probably ascribable to the MgO phase. In these two spectra (Figs. 5d, 5e), a broad weak band was observed at 960 cm^{-1}, which has been assigned to Mg pyrovanadate in Ref. 3. This assignment is questionable, since there is no indication of the presence of Mg pyrovanadate at Mg/V $\geq 3/2$; only Mg orthovanadate and/or Mg oxide are detected. This weak band is probably associated with the structural distortion of Mg orthovanadate due to the presence of excess Mg oxide. At even higher Mg content, a strong broad band at 481 cm^{-1} due to the MgO phase appears (Fig. 5f). However, the V–O vibrational band still exists at $\sim$834 cm^{-1}. The FT-IR analysis confirms well the results by XRD analysis.

The double bands of Mg pyrovanadate at 976 and 969 cm^{-1} display interesting features at different Mg/V ratios. In the V-rich catalyst (Mg/V = 3/4) the double bands are well defined, but they are not resolved in the Mg-rich catalyst (Mg/V = 5/4) and they appear as a single peak at 975 cm^{-1}.

Raman study. The Raman spectra of (1/2)MgVO, (1/1)MgVO, and (3/2) MgVO are presented in Fig. 6. They

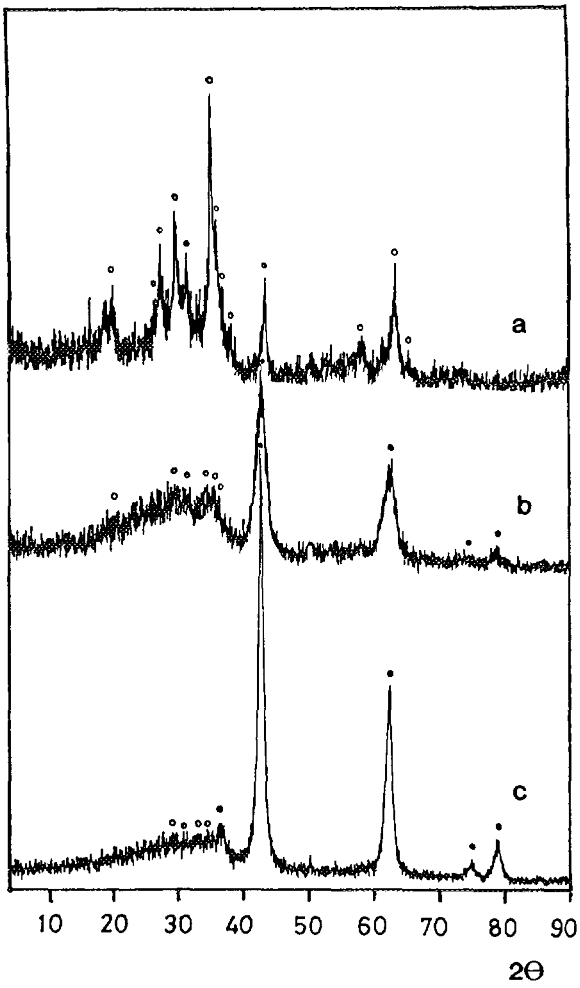

FIG. 3. X-ray diagrams of (a) (7/4)MgVO, (b) (4/1)MgVO, (c) (9/1)MgVO. (○) $Mg_3V_2O_8$, (●) MgO.

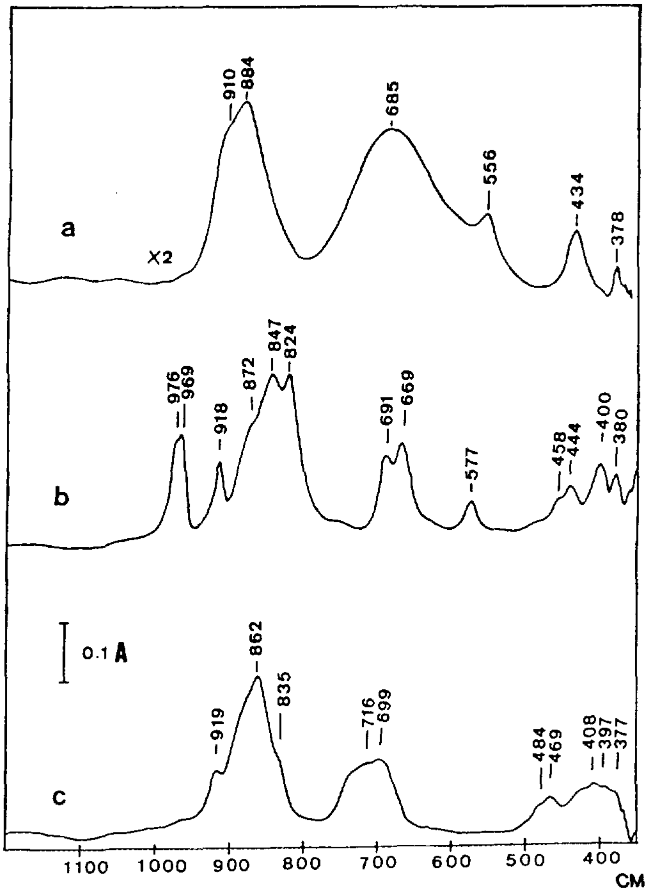

FIG. 4. Infrared spectra of (a) (1/2)MgVO (MgV_2VO_6), (b) (1/1)MgVO ($\alpha Mg_2V_2O_7$), (c) (3/2)MgVO ($Mg_3V_2O_8$).

correspond to the pure MgV_2O_6, α-$Mg_2V_2O_7$, and $Mg_3V_2O_8$ phases, respectively (6). For the (1/2)MgVO catalyst, a very weak band was observed at ~993 cm^{-1} due to V_2O_5 oxide. Since the Raman cross section of V_2O_5 oxide is much larger than that of the metavanadate phase (see below), the relative amount of V_2O_5 impurity in the (1/2)MgVO catalyst must be very small. In the spectrum of the (3/2)MgVO catalyst, a very weak band at ~902 cm^{-1} was observed due to a very small quantity of Mg pyrovanadate impurity.

The Raman spectra of (1/4), (3/4), and (5/4)MgVO catalysts are shown in Fig. 7. The (1/4)MgVO catalyst, which consists of theoretically identical phase ratios of vanadium oxide and Mg metavanadate, exhibits strong Raman bands at 994, 700, 527, 482, 404, 304, 284, 198, and 145 cm^{-1} due to V_2O_5 oxide, and weak bands at 920, 835, 730, and 404 cm^{-1} due to the Mg metavanadate phase. This result indicates that the Raman cross section of V_2O_5 oxide is much larger than the cross section of Mg metavanadate phase. The (3/4)MgVO catalyst containing theoretically identical phase ratios of Mg metavanadate and pyrovanadate exhibits very strong bands mainly at 920, 835, 730, 439, 175, and 150 cm^{-1} due to Mg metavanadate phase, and weak bands at 947, 901, 872, and 620 cm^{-1} due to Mg pyrovanadate phase, indicating that the Raman cross section of Mg metavanadate is much larger than that of the pyrovanadate phase. The Raman spectrum of the (5/4)MgVO catalyst displays strong bands both at 947 and 901, and 860 and 826 cm^{-1}, which are due to Mg

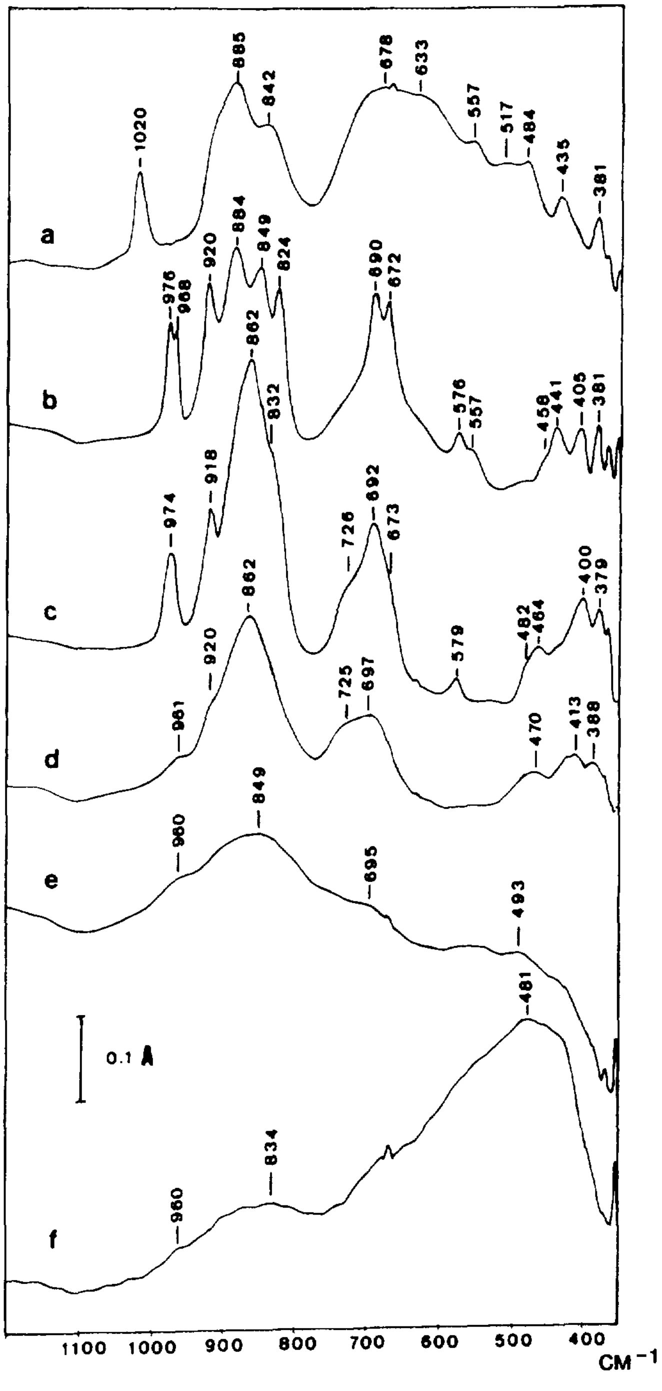

FIG. 5. Infrared spectra of (a) (1/4)MgVO, (b) (3/4)MgVO, (c) (5/4)MgVO, (d) (7/4)MgVO, (e) (4/1)MgVO, (f) (9/1) MgVO.

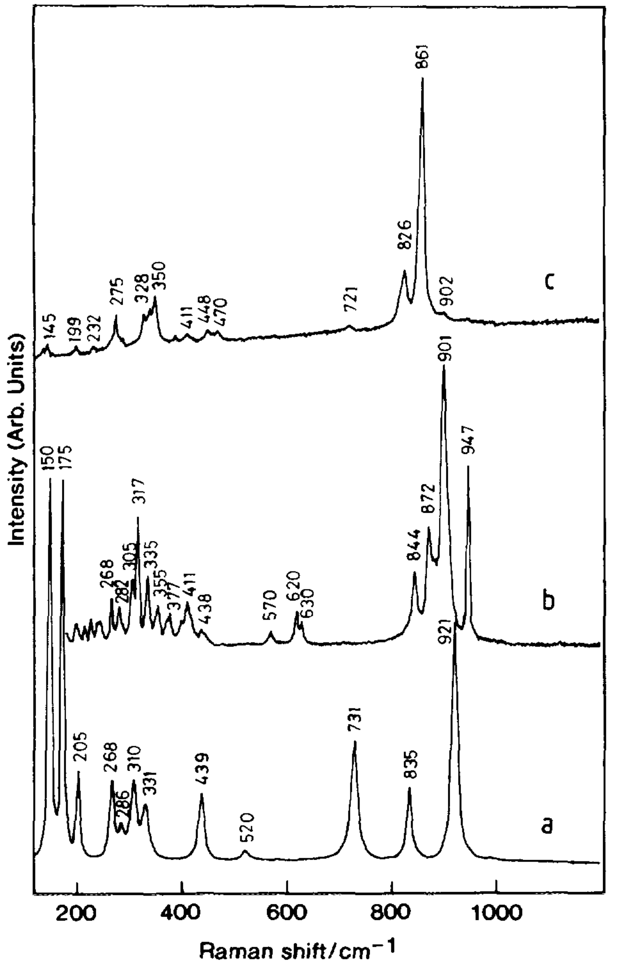

FIG. 6. Raman spectra of (a) (1/2)MgVO (MgV_2O_6), (b) (1/1) MgVO ($\alpha Mg_2V_2O_7$), (c) (3/2)MgVO ($Mg_3V_2O_8$).

pyrovanadate and orthovanadate phases, respectively. For (7/4), (4/1), and (9/1)MgVO catalysts, no Raman spectra were obtained due to very strong fluorescence.

The catalysts after reaction have also been examined, and no appreciable structural change was observed by XRD, FTIR, or Raman techniques.

XPS measurement. The XPS results concerning surface composition and B.E. of oxygen, vanadium, and magnesium of some catalysts are reported in Table 3. References NH_4VO_3, V_2O_5, and V_2O_4 (p.a., Janssen Chimica) were used to determine the $V_{2p_{3/2}}$ binding energy corresponding to V^{5+} and V^{4+}. Their spectra are shown in Fig. 8, and their B.E. are given in Table 3. It is observed from Fig. 8 that the V_2O_4 sample apparently contained some V_2O_5, due to the oxidation of V_2O_4 by oxygen on exposure to air. On each sample measured, two B.E. for $V_{2p_{3/2}}$ were obtained in the regions 517.1–517.6 and 515.4–515.6 eV. Some examples of XPS spectra obtained are presented in Fig. 8.

The assignment of bands is a very complex problem, as can be seen from the different results reported in literature. For example, for V_2O_3, values for B.E. of 513.1, 515.7, and 515.8 eV have been assigned (11–13). For V_2O_4, binding energy values of 515.5, 515.7, and 516.3–516.6 eV have been assigned (12–15), and for V_2O_5, values between 517.1 and 518 eV have been assigned (3, 15–18). In addition, it should be noted that a low binding energy band (515.4 eV) was observed in commercial reference V_2O_5 oxide, similar to our prepared V_2O_5 oxide. It can be suggested that bands with a high binding energy value can be assigned to the presence of V^{5+}, and that those with a low binding energy value could be an indication of the presence of some reduced vanadium species, probably V^{4+}. Taking into account the limitation in the assignment of the bands, an approximate estimate of the V^{5+}/V^{4+} surface atomic ratios can be made using the XPS technique. The results obtained for fresh catalysts are presented in Table 3. Similar results are obtained for used catalysts. From these V^{5+}/V^{4+} atomic ratios, it can be

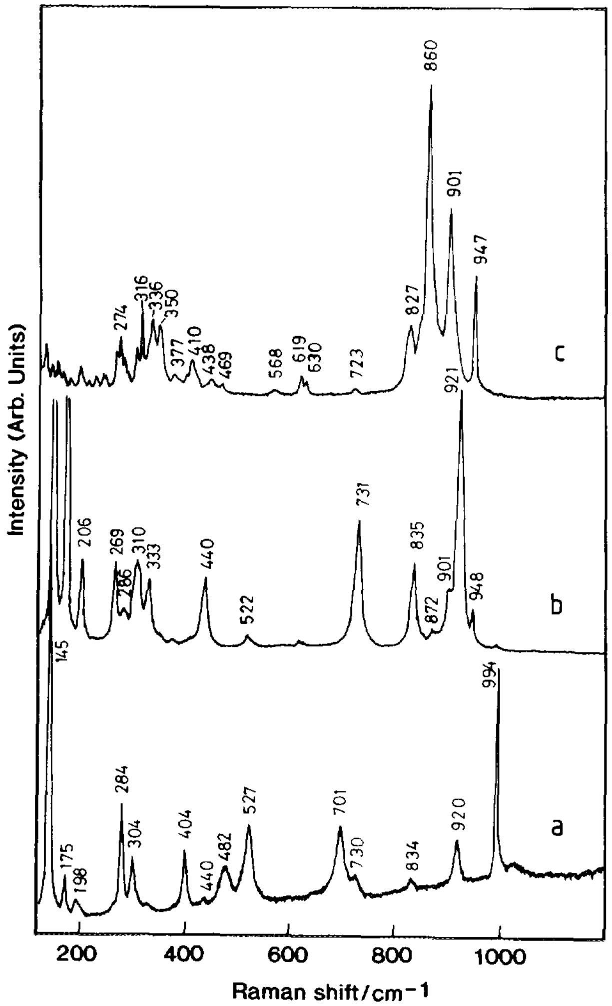

FIG. 7. Raman spectra of (a) (1/4)MgVO, (b) (3/4)MgVO, (c) (5/4)MgVO.

TABLE 3

The XPS Results for V–Mg–O Catalysts

Samples	$B.E_L V_{2P_{3/2}}$	$B.E_L V'_{2P_{3/2}}$	$B.EO_{1S}$	$B.EMg_{2S}$	V^{5+}/V^{4+}	Mg/O	V/O	Mg/V
NH_4VO_3	517.6						0.33	
V_2O_4	517.2	515.6	530.1		3.52		0.35	
V_2O_5	517.3	515.4	530.2		16.44		0.34	
(1/2)MgVO	517.3	515.4	530.1	89.1	9.54	0.21	0.29	0.73
(3/4)MgVO	517.4	515.6	530.3	88.9	9.14	0.29	0.27	1.11
(1/1)MgVO	517.4	515.6	530.2	88.7	11.87	0.34	0.25	1.34
(5/4)MgVO	517.3	515.6	530.0	88.5	10.10	0.40	0.22	1.79
(3/2)MgVO	517.1	515.4	529.9	88.4	9.36	0.44	0.20	2.20
MgO			529.4	87.9		0.85		
MPO	517.1	515.4	530.0	88.4	9.55	0.41	0.21	1.93
(1/1)MgVO[a]	517.5	515.7	530.4	88.8	11.3	0.34	0.25	1.34
(1/1)MgVO[b]	517.5	515.7	530.3	88.8	12.79	0.35	0.25	1.40

[a] Sample after reaction: T = 540°C, C_3H_8/O_2 = 8%/4%, 20 h.
[b] Sample after reaction: T = 540°C, C_3H_8/O_2 = 8%/2%, 20 h.

argued that in spite of the great difference between catalyst composition, the V^{5+}/V^{4+} surface atomic ratios were constant (around 10), indicating that probably this ratio has little relation to bulk compositions. These results suggest that the small amount of reduced vanadium species, probably V^{4+}, on the catalyst surface does not directly reflect properties of the samples, and that they are probably produced during XPS measurement due to the high vacuum under which samples have been pretreated ($<10^{-9}$ Torr).

The mechanical mixture MPO has also been examined. Its Mg/V surface atomic ratio (1.93) is larger than the mean value (1.77) of (1/1)MgVO (1.34) and (3/2)MgVO (2.20), and also larger than that of (5/4)MgVO (1.79). It is more typical of the value of (3/2)MgVO. Even if these differences are not significant, this observation can be explained in two ways. First, it has been reported (19) that in a mechanical mixture containing two phases, the surface composition measured by XPS can be affected by the difference of particle size between two phases. In the case of MPO, the particle size of (3/2)MgVO formed on the surface of the mixture should be smaller (the S_{BET} of the (3/2)MgVO catalyst prepared separately was 22.8 m^2/g) than that of (1/1)MgVO (the S_{BET} of the (1/1)MgVO catalyst prepared separately was 8.3 m^2/g). Therefore, the surface of (3/2)MgVO particles accessible to XPS analysis should be higher than that of (1/1)MgVO, resulting in a surface composition of MPO more representative of the (3/2)MgVO catalyst.

The second explanation would be a surface enrichment in Mg, as has been reported previously (3). We cannot exclude this last possibility, but taking into account the fact that the mechanical mixture has been prepared by mixing the catalysts prepared separately, and that during the preparation of the mechanical mixtures the temperature was never higher than 80°C, this possibility, or another type of contamination, does not seem plausible. After catalytic reaction, no appreciable change was observed in the surface compositions and B.E. of Mg, V, and O elements of MPO, suggesting that the solid state reaction between (1/1)MgVO and (3/2)MgVO does not occur during the test.

The surface composition for fresh catalysts is presented in Table 3. Similar results are observed for used catalysts. As an example, Fig. 8 shows the XPS spectra of (1/1)MgVO before and after reaction. From Table 3, it can be seen that even under very low oxygen concentration (8% C_3H_8 and 2% O_2) the surface composition did not show any noticeable change after reaction.

Catalyst Test

The results of the catalyst tests of V–Mg–O catalysts at 500 and 540°C are presented in Table 4, in which selectivity and yield concern the formation of propene. Oxidative dehydrogeneration and combustion are the major reactions. V_2O_5 is active, but its selectivity for propene is low. MgO is neither active nor selective. All the V–Mg–O catalysts are more selective than the simple oxides.

No clear trend appears when the overall conversion is considered. However, the conversion per surface area decreases with increasing Mg/V ratio. The higher yields were then obtained with (5/4), (7/4), (4/1), and (9/1)MgVO catalysts, which are due to both relatively large values of activity and selectivity.

Table 5 compares the different V–Mg–O catalysts at similar conversions. The higher values in selectivity were observed for (1/1), (5/4), (7/4), and (4/1)MgVO and mechanical mixture MPO. The selectivity of these samples is, in all cases, about 53–56%. These values are signifi-

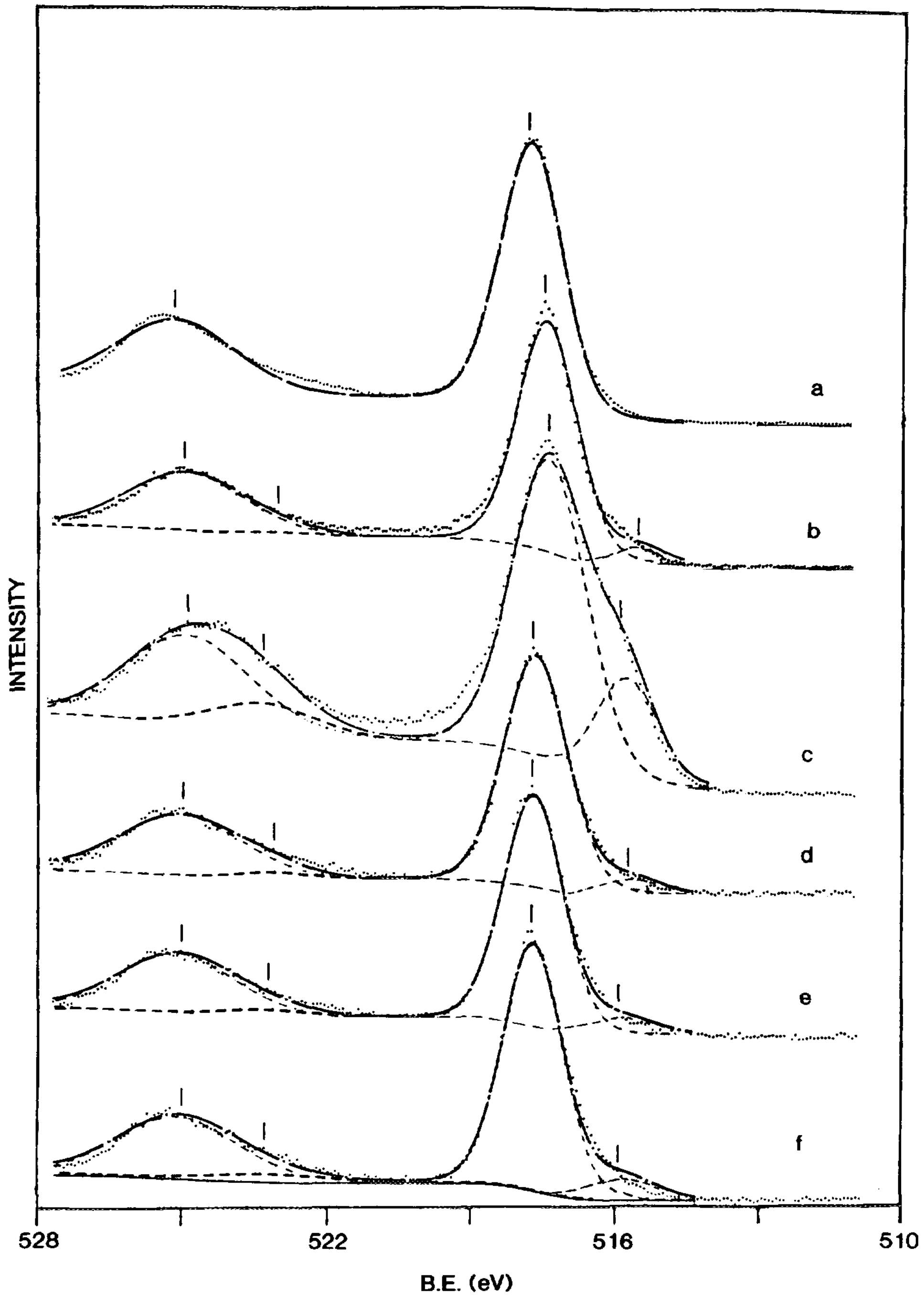

FIG. 8. XPS spectra of (a) NH_4VO_3, (b) V_2O_5, (c) V_2O_4, (d) (1/1)MgVO before reaction, (e) (1/1)MgVO after reaction at 540°C for 20 h. C_3H_8/O_2 = 8%/4%. (f) (1/1)MgVO after reaction at 540°C for 20 h. C_3H_8/O_2 = 8%/2%.

cantly higher than those obtained for all of the other samples (about 45%).

An experiment aimed at correlating propene selectivity with propane conversion was carried out by changing the catalyst weight. On all the catalysts tested, the selectivity decreased with increasing conversion, in agreement with previous publications (2, 3).

Figure 9 illustrates the curves for the (1/2), (3/4), (1/1), and (3/2)MgVO catalysts. It can be seen that (1/1)MgVO (pure α-$Mg_2V_2O_7$ phase) has the best selectivity for propene; (3/2)MgVO (pure $Mg_3V_2O_8$ phase) is in the middle; (1/2)MgVO (pure MgV_2O_6) is worst, and its selectivity decreases more rapidly as the propane conversion increases. The (3/4)MgVO catalyst, which consists of Mg

TABLE 4

Catalytic Results for Propane Oxidation over V–Mg–O Catalysts

Catalysts	Reaction T = 500°C				Reaction T = 540°C			
Mg/V (atomic ratio)	C(%)	Cm^{-2}	S(%)	Y(%)	C(%)	Cm^{-2}	S(%)	Y(%)
V_2O_5	14.1	20.4	30.7	4.3	22.6	32.8	27.9	6.3
(1/4)MgVO	17.4	17.1	51.3	8.9	21.6	21.3	44.9	9.2
(1/2)MgVO	13.1	16.2	68.2	9.0	18.1	22.3	55.4	10.0
(3/4)MgVO	21.9	9.0	52.0	11.0	30.2	12.4	37.3	11.3
(1/1)MgVO	20.3	8.1	62.3	12.6	27.1	10.9	53.2	14.4
(5/4)MgVO	22.5	5.4	59.8	13.4	32.5	7.8	47.1	15.3
(3/2)MgVO	24.0	3.5	46.6	11.2	32.3	4.7	40.9	13.2
(7/4)MgVO	22.2	2.1	59.6	13.2	32.2	3.0	48.2	15.5
(4/1)MgVO	25.9	1.6	52.4	13.6	46.0	2.8	35.7	16.4
(9/1)MgVO	43.0	1.1	34.5	14.8	53.2	1.4	30.3	16.1
MgO	3.7	0.2	—	—	7.9	0.3	3.4	0.3

Note. Propane/O_2 = 4%/8%, catalyst weight = 0.300 g.

metavanadate and pyrovanadate phases, was more active than either (1/2)MgVO or (1/1)MgVO, but its selectivity was low, similar to that of (1/2)MgVO.

For a given conversion, the propene selectivities over (5/4)MgVO and (7/4)MgVO catalysts were higher than any of the pure Mg vanadate phases; see Fig. 10. These two catalysts correspond to mixtures of the Mg pyrovanadate and orthovanadate phases, and orthovanadate with excess Mg oxide, respectively. The same selectivity versus conversion curve was also obtained with higher Mg content ((4/1)MgVO).

To investigate a possible promotion effect on selectivity over biphasic catalysts, mechanical mixtures of MPO and MOM were examined. Figure 11 shows the selectivity as a function of conversion on these two mixtures. For MPO, i.e., mechanically mixed α-$Mg_2V_2O_7$ and $Mg_3V_2O_8$ phases, the selectivity is about the same as (1/1)MgVO. This result suggests that the selectivity of $Mg_3V_2O_8$ phase can be promoted by a mechanically mixed α-$Mg_2V_2O_7$ phase.

TABLE 5

Comparison of Propene Selectivities at Similar Conversions

Catalysts	Wt(g)	C(%)	S(%)
(1/2)MgVO	0.5	24.0	44.4
(3/4)MgVO	0.2	24.4	47.0
(1/1)MgVO	0.25	24.5	56.2
(5/4)MgVO	0.2	26.1	56.2
(3/2)MgVO	0.15	23.6	49.6
	0.2	26.8	45.6
(7/4)MgVO	0.2	26.0	56.5
(4/1)MgVO	0.1	27.2	53.0
MPO	0.2	24.6	55.4
MOM	0.4	23.9	49.0

Note. Propane/O_2 = 4%/8%, T = 540°C.

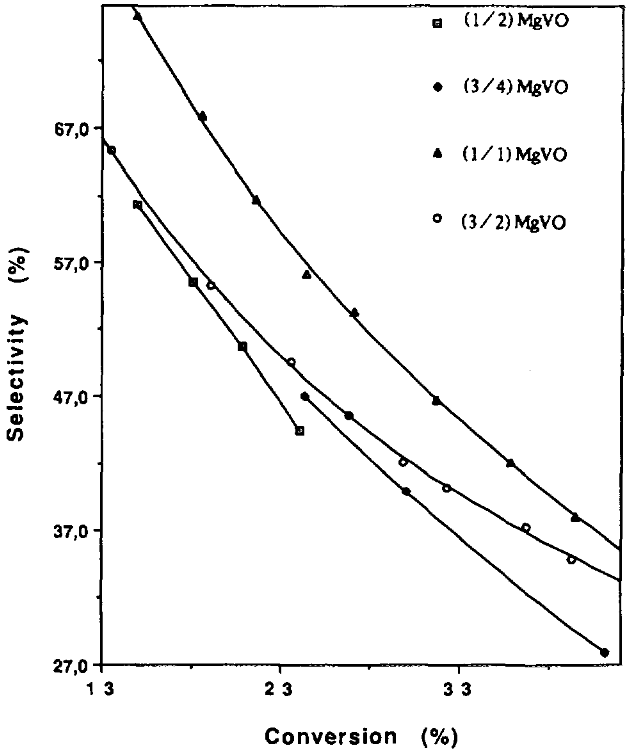

FIG. 9. Propene selectivity as a function of propane conversion. Catalytic conditions: T = 540°C; propane/oxygen = 4%/8%, and total flow rate = 50 ml/min, catalyst weight between 0.100 g–0.600 g.

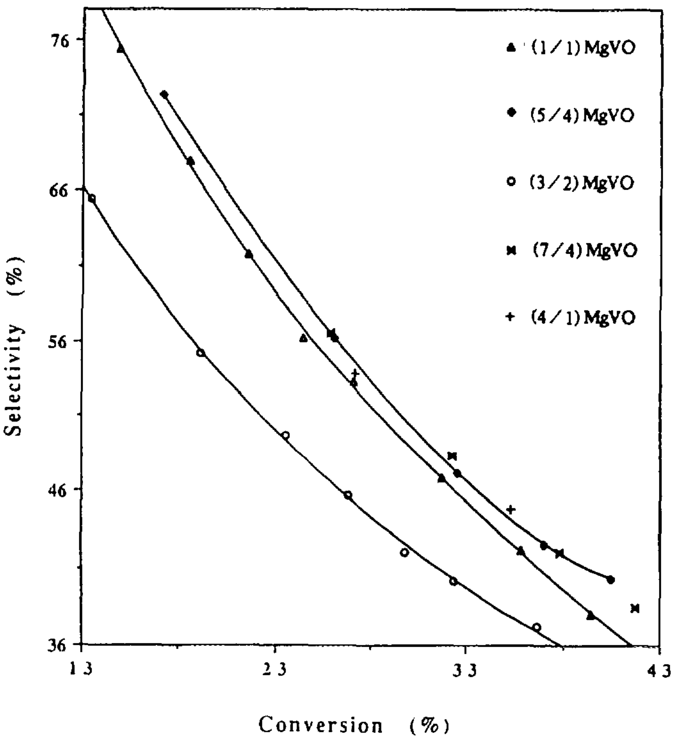

FIG. 10. Propene selectivity as a function of propane conversion.

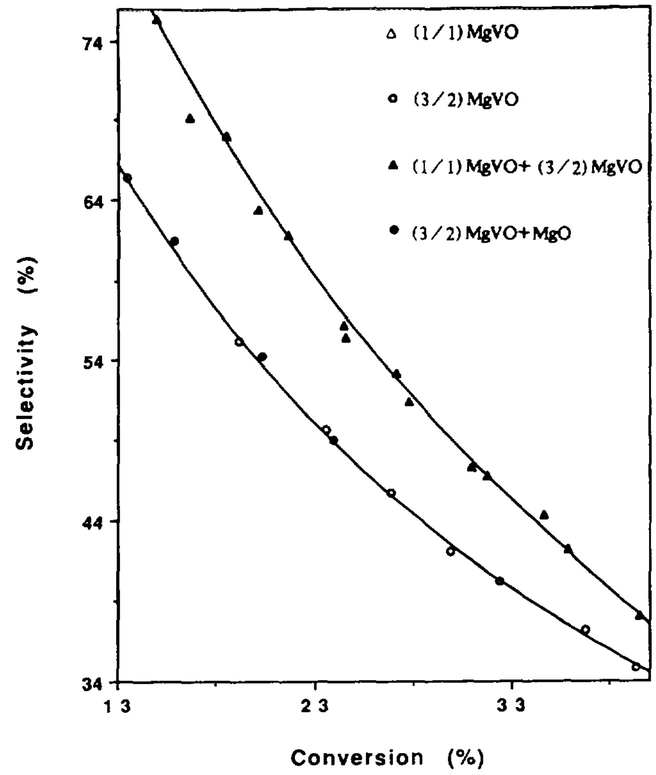

FIG. 11. Propene selectivity as a function of propane conversion.

In contrast, no promotion effect on the selectivity of (3/2)MgVO was observed over the mechanical mixture MOM. Since the MgO phase exhibits very low activity, the overall catalytic performance is about the same as (3/2)MgVO, independent of the presence of the MgO phase.

DISCUSSION

Concerning catalyst activity, three contributing factors should be considered jointly, i.e., the surface area of a catalyst, the density of active sites, and the specific reactivity of active sites. As shown in Table 1, the surface area of V–Mg–O catalysts generally increases with increasing Mg content. However, the catalytic results in Table 4 show that the conversion per surface area tends to decrease with increasing Mg content. This indicates that the specific activity of V–Mg–O catalysts depends on the density of V ions. The lower the V content, the lower the specific activity of a catalyst. This fact clearly confirms the previous conclusion that vanadium ions act as active sites for propane oxidation (2, 3).

In the oxidative dehydrogenation of propane, the propene selectivity generally decreases with increasing conversion. This phenomenon is due largely to secondary reactions, as was found in many other alkane oxidations (20). Published results have shown that on V–Mg–O catalysts, the product distribution is only slightly affected by the reaction temperature, and changing the oxygen/alkane ratio in the feed by a factor of 4 results in only small changes in the product distribution (2, 21). Our results show that other phenomena, not considered up to now in the literature, could play a role in explaining selectivity in propene oxidative dehydrogenation. It can be suggested that the presence of more than one phase can promote selectivity. We are investigating this possibility in detail, and it seems to be confirmed. However, taking into account the results presented in this work, it is only a suggestion. In spite of the fact that the increase in selectivity is not very significant, the results are very indicative. The highest selectivity at a given conversion was observed on the biphasic catalysts, i.e., (5/4)MgVO and (7/4)MgVO. The former is the phase mixture of Mg pyrovanadate and orthovanadate with theoretical molar phase ratio equal to 1. Its surface Mg/V ratio shown in Table 3 is about the average value between (1/1)MgVO and (3/2)MgVO, indicating that the pyrovanadate and orthovanadate phases are exactly distributed in the (5/4)MgVO catalyst. Since the specific activity of the pyrovanadate phase is higher than that of the orthovanadate phase due to its relatively high V content, the overall catalytic behavior of the (5/4)MgVO catalyst should be more representative of the pyrovanadate phase. However, the selectivity of propene over the (5/4)MgVO catalyst is higher than the pure α-$Mg_2V_2O_7$ phase itself, suggesting that a promotion effect might exist between the two phases. The results observed in the mechanical mixture of (1/1)MgVO and (3/2)MgVO seem to confirm that some phenomena linked to the presence of two MgVO phases may be found in these types of catalysts. In the mechanical mixture, the selectivity is about the same as that of (1/1)MgVO, rather than the average, indicating that the simultaneous presence of α-$Mg_2V_2O_7$ and $Mg_3V_2O_8$ leads to an increase of the selectivity of the mixture.

For the (7/4)MgVO catalyst, which consits of Mg orthovanadate with excess Mg, the promotion effect on selectivity seems different. The mechanically mixed MgO did not enhance the propene selectivity of (3/2)MgVO. Here, it is worthwhile to discuss the structure of (7/4)MgVO catalyst. Both XRD and FT-IR techniques did not detect the presence of the crystalline MgO, but the broadened peaks and poor resolved spectra of the Mg orthovanadate phase reveal the contribution from excess Mg oxide. Taking into account the fact that catalyst preparation with the citrate method gives a very homogeneous Mg–V precursor, this catalyst could, in principle, be a solid solution of Mg oxide in the orthovanadate phase. However, the structure of the Mg orthovanadate is orthorhombic, which is very different from the cubic structure of the MgO phase. Hence, it is hard to define whether the catalyst is composed of isolated, very highly dispersed, poorly crystallized Mg oxide, or an orthovanadate possessing some position which is defective in vanadium ions. But the increase in selectivity of propene on (7/4)MgVO compared to mechanically mixed (3/2)MgVO + MgO reflects that the intimate contact of the orthovanadate phase with excess Mg, or even the MgO phase, is favorable. This result is in agreement with the previous observation by Kung and co-workers (22). The catalytic behavior of (7/4) MgVO is somewhat similar to that of the VPO catalyst, in which a slight excess of phosphorous is more selective than a stoichiometric vanadyl pyrophosphate (23, 24).

In a previous study by Kung and co-workers (1, 25), the V–Mg–O catalysts were prepared by impregnation of ammonia metavanadate on MgO support. This method provided the possibility that the orthovanadate phase could coexist with Mg oxide. But a straightforward interpretation is difficult, as in the preparation of this pure phase. The authors detected a small amount of pyrovanadate (21). Our results presented above have shown that the pure $Mg_3V_2O_8$ phase itself is not very selective, but the modification by coexisting pyrovanadate or excess Mg oxide can result in a relatively high propene selectivity.

It should be noted that the (3/4)MgVO catalyst with mixed metavanadate and pyrovanadate phases, exhibits a low selectivity, more representative of a pure MgV_2O_6 phase, as shown in Fig. 9. Evidently, due to the higher V content, the specific activity of the Mg metavanadate phase should be higher than that of Mg pyrovanadate. Since the citrate method provides a homogeneous distribution of these two phases in the catalyst, as evidenced also by XPS results, a stronger influence of the metavanadate phase on the overall catalytic performance should result. This result indicates that much care should be taken when using solid–solid reaction to prepare the pure Mg pyrovanadate. If the reaction does not go to completion, the strong influence of coexisting Mg metavanadate could play a decisive role, especially when it exists around the surface. The catalytic performance will then be very different from that of the pure compound.

The V–Mg–O catalysts prepared by Volta and co-workers (3) are generally mixtures of several phases, with sometimes even four phases coexisting in a single catalyst. In addition to the possible negative influence of residual potassium (21), the complexity of the phases in the catalyst makes it hard to tell which phase is really active or selective.

The explanation of the promotion effect is being investigated. At present four principal reasons can explain such a promotion: first, the formation of new structures (not observed during characterization of the catalysts) between the two observed phases; second, the depostion (or transfer) of magnesium from the rich phase to the Mg-poor phase (namely contamination between the phases); third, some epitaxial phenomena between both Mg vanadate phases or between Mg vanadate and MgO phases; and fourth, a cooperative effect between two uncontaminated Mg vanadate phases (namely as external phases) via oxygen spillover (remote control effect).

One (or several) of these explanations, together with the modifications of the redox properties, the basicity, and probably the type of oxygen involved in the dehydrogenation, should be considered to explain the above results completely.

The promotion of selectivity of the (3/2)MgVO catalyst by the gently mechanically mixed (1/1)MgVO as an external phase plays a role that could be a remote control effect.

The present results clearly show that among the three pure Mg vanadate phases, the Mg pyrovanadate phase is the most selective for propene, in agreement with the results obtained by Volta *et al.* (3). However, in the V–Mg–O catalysts, which possess more than one phase together, their catalytic behaviors are much different from that of the corresponding pure phases. Our results point to the fact that the presence of a secondary Mg vanadate phase could be very important in explaining the catalytic behavior of V–Mg–O catalysts, and that the detailed knowledge of one single crystallographic phase is probably insufficient to allow us to predict the catalytic performance of these types of catalysts.

The results obtained suggest that the phase purity affects the catalytic behavior of the Mg vanadate phase. The presence of one phase is not sufficient to explain the catalytic performance of the V–Mg–O catalysts. Some type of cooperation, probably between external and noncontaminaed phases, exists in these types of catalysts.

CONCLUSION

The citrate method is a good way to prepare V–Mg–O catalysts with controlled phase formation.

The dependence of the specific activity of V–Mg–O catalysts on the vanadium content confirms that the vanadium ions act as active sites for propane oxidation.

The catalytic performance of the biphasic V–Mg–O catalysts are much different from that of the corresponding pure phases. The selectivity of the Mg orthovanadate phase can be improved by the coexisting pyrovanadate phase or excess Mg and Mg oxide phases, suggesting that some synergy effect might exist between the phases. When the Mg pyrovanadate phase coexisted with the metavanadate phase, the overall catalytic performance was more typical of metavanadate. The results obtained suggest that the phase purity affects the catalytic behavior of the Mg vanadate phase. The presence of one phase is not sufficient to elucidate the catalytic performance of the V–Mg–O catalysts.

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