Catalysis Letters Vol. 86, No. 4, March 2003 (© 2003)

Effect of modifiers on the reactivity of Cr_2O_3/Al_2O_3 and Cr_2O_3/TiO_2 catalysts for the oxidative dehydrogenation of propane

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Received 16 July 2002; accepted 29 November 2002

Chromium oxide supported on alumina and titania supports was modified with oxides of sodium, vanadium and molybdenum. The modified and unmodified chromium oxide catalysts were characterized by several techniques. The presence of surface chromium oxide and surface molybdenum and vanadium oxide species was detected in the unmodified and molybdenum and vanadium oxide modified supported chromium oxide catalysts. The reducibility (T_{max} and H/Cr ratio) of the surface chromium species was not affected for the vanadium and molybdenum oxide modified catalysts; however, the reducibility changed noticeably for sodium modified supported chromium oxide catalysts. Studies of the reactivity of the ODH of propane revealed the effect of modifiers on the reactivity properties of the surface chromium oxide species. The activity and propene selectivity decreased for sodium modified supported chromium oxide catalysts. However, the activity increased for vanadium oxide modified catalysts and was similar for molybdenum oxide modified catalysts irrespective of the support. The propene selectivity was higher for molybdenum oxide modified chromium oxide catalysts. However, the propene selectivity for vanadium oxide modified catalysts depends on the support since it appears that the inherent selectivity of the surface vanadium oxide species is reflected.

KEY WORDS: chromia; TiO_2; Al_2O_3; modifiers; MoO_3; WO_3; oxidative dehydrogenation of propane; Raman; EPR; TPR; XRD.

1. Introduction

Recently, the oxidative dehydrogenation (ODH) of alkanes has received considerable attention owing to the thermodynamic and economic constraints of the dehydrogenation reactions [1,2]. Supported metal oxide catalysts have been extensively used to study the effectiveness of the ODH reaction [3–8]. Supported chromium oxide catalysts are also effective catalysts for the ODH of propane [9–16]. These studies reveal that the oxide support plays an important role. Among the supported chromium oxide catalysts the specific activity of the surface chromium oxide species follows the order $Cr_2O_3/TiO_2 \sim Cr_2O_3/SiO_2 > Cr_2O_3/SiO_2–Al_2O_3 > Cr_2O_3/Al_2O_3$ [16]. Similarly to supported vanadium oxide catalysts, the propene selectivity is low for the Cr_2O_3/TiO_2 catalyst compared with the higher selectivity obtained on the less active Cr_2O_3/Al_2O_3 catalysts. Therefore, it is essential to design a catalyst that optimizes both conversion and selectivity of ODH reactions.

It has been reported that addition of acidic surface metal oxides (W, Nb, P) to supported metal oxides increases the selectivity for selective oxidation reactions [17–20]. Moreover, the activity decreased if Li, Na and K were added to supported metal oxides [21] for the ODH of propane. Studies on the physicochemical and catalytic properties of chromia/vanadia catalysts supported on TiO_2 for the SCR of NO_x with NH_3 suggested that an optimum composition of the Cr and V sites over TiO_2 was required to achieve the best catalytic performance [22,23]. The enhanced catalytic performance was due to a synergic effect developed between Cr and V sites. El-Idrissi *et al.* reported the effect of modifying Cr/TiO_2 catalysts with phosphorus for the ODH of ethane [24]. An optimum P/Cr value at which the conversion and selectivity are maximum was reported. Flick and Huff studied a $Pt–Cr/TiO_2$ catalyst for the ODH of ethane and observed higher activity due to the presence of Pt [25]. Grabowski *et al.* studied the ODH of isobutane for chromium oxide supported on different metal oxides modified with potassium [26]. They reported that the selectivity and activity depend upon the nature of support and amount of potassium present. Smits *et al.* studied the ODH of propane over different compositions of Cr and V over an Nb_2O_5 support [27]. The conversion was observed to increase with increase in the amount of Cr and V, but the selectivity was inversely proportional to conversion. Deo and Wachs classified the modifiers/additives as interacting or non-interacting depending on whether the modifiers change the structure and reactivity of the surface vanadium oxide species [28].

Since supported chromium oxide catalysts are known to be effective for the ODH of propane and because of the sparsity of studies dealing with modified supported chromium oxide catalysts, it appeared worthwhile to

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1011-372X/03/0300-0179/0

study the effect of modifiers on these catalysts. This was the primary objective of the present study. To achieve this objective, several modifiers were considered. The modifiers were chosen such that they were interacting and non-interacting in nature. The modifiers considered were oxides of sodium, vanadium and molybdenum. The catalysts to be modified were sub-monolayer chromium oxide supported on alumina and titania supports. The modified and unmodified catalysts were synthesized and characterized by various techniques. Finally, the catalysts were used for the ODH of propane and the effect of the modifiers was determined.

2. Experimental

2.1. Catalyst preparation

Alumina and titania supported chromium oxide catalysts were prepared by the incipient wetness impregnation technique. The precursor used was chromium nitrate nonahydrate [$Cr(NO_3)_3 \cdot 9H_2O$, Aldrich, 99.98% purity] and the supports were alumina (Condea) and titania (P-25, Degussa). Based on the detailed procedure given elsewhere [16], 5 wt% Cr_2O_3 on Al_2O_3 and 1 wt% Cr_2O_3 on TiO_2 catalysts were prepared and denoted CrAl and CrTi, respectively.

The synthesized CrAl and CrTi catalysts were modified with sodium, vanadium and molybdenum oxides. The modified catalysts were prepared by a second impregnation procedure. The precursors used for sodium, vanadium and molybdenum oxides were NaOH (20% solution), ammonium metavanadate (NH_4VO_3, CDH, 98%) + oxalic acid (1:2 mole ratio), and ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24} \cdot 2H_2O$, Alfa products], respectively. Sodium modified CrAl catalysts were prepared by adding known amounts of aqueous NaOH solutions corresponding to Na/Cr weight ratios of 0.02, 0.06, 0.1 and 0.15 to the previously prepared CrAl sample. The samples were denoted Na_xCrAl, where x correspond to the Na/Cr weight ratio. Similarly, the other modified CrAl catalysts were prepared by adding the required amount of precursor solution corresponding to 8.8 wt% V_2O_5 and 10 wt% MoO_3. The samples were denoted VCrAl and MoCrAl, respectively. The modified CrTi catalysts were prepared by adding the required amount of precursor solution corresponding to 0.06 wt% Na_2O, 2 wt% V_2O_5 and 2 wt% MoO_3 to the prepared 1 wt% Cr_2O_3/TiO_2 samples and are denoted $Na_{0.6}$CrTi, VCrTi, and MoCrTi, respectively. The precursor solution and CrAl or CrTi samples were mixed thoroughly and dried at room temperature. The samples were further dried overnight at 383 K and finally calcined at 773 K for alumina supported samples and at 723 K for titania supported samples for 6 h. To understand the effect of the additives, 10 wt% MoO_3 on Al_2O_3 support and 2 wt% MoO_3 on TiO_2 support were prepared by adding the required amount of precursors and following the above heat treatment procedure.

2.2. Surface area

The surface areas of the samples were obtained using the single point BET method. A bench-top Coulter SA 3100 apparatus using N_2 adsorption at 77 K was used for this purpose.

2.3. XRD

X-ray diffraction (XRD) patterns were obtained on a 180 Debye Flex-2002 X-ray diffractometer using Ni filtered Kα radiation from a Cu target ($\lambda = 1.54056$ Å) and equipped with a monochromator.

2.4. Raman spectroscopy

Laser Raman spectroscopy studies of the CrAl and CrTi catalysts and those modified with sodium, vanadium and molybdenum under ambient conditions were performed with an argon ion laser (Spectra Physics, Model 165). About 200 mg of the supported chromia catalysts were pressed into self-supporting wafers and placed in a sample cell. Additional details can be found elsewhere [29].

2.5. Electron paramagnetic resonance (EPR)

Electron paramagnetic resonance studies were performed on a Varian E-109 X-band spectrometer. The spectra were obtained at room temperature using a microwave frequency of ~9.15 GHz and a microwave power of 10 mW. The scan time was 8 min and the magnetic field modulation frequency was 100 kHz. The EPR spectra were calibrated with DPPH using a dual cell.

2.6. Temperature-programmed reduction (TPR)

TPR studies were carried out in a microreactor containing ~0.05 g of catalyst and attached to a Micromeritics Pulse Chemisorb 2705 analyser. A 10% H_2–Ar mixture flowing at 40 sccm was used for reduction on previously degassed samples and the temperature was ramped at a rate of 10 K/min from ~373 to 973 K. The amount of hydrogen consumed was detected using a thermal conductivity detector. Additional details can be found elsewhere [15].

2.7. Oxidative dehydrogenation of propane

The samples were tested for the ODH of propane in a vertical down-flow quartz reactor at atmospheric pressure. The reactor was a single quartz piece mounted vertically in a tubular furnace. The temperature of the catalyst bed was measured with a thermocouple and controlled by a PID controller (Fuji Micro-controller X Model PXZ 4). The product gases were sent for on-line analysis to a gas chromatograph (Aimil-Nucon 5765) equipped with a methanizer and a flame ionization detector (FID). The carbon oxides and hydrocarbons were separated using an activated alumina column (length 25 cm) and detected with the FID. The propane flow rate was adjusted through a thermal mass flow controller (Bronkhost Hi-Tec, Model F-201D FAC-22-V) and the air flow rate was adjusted through a rotameter (Eureka, Model SRS/MG-5) to maintain a 3:1 propane to oxygen ratio. A physical mixture of 0.1 g of the catalyst and the required amount of quartz glass powder to form a bed height of 1 cm was loaded into the reactor. Runs were performed at different temperatures starting from 573 to 723 K with a constant total flow rate of 42.7 sccm. The conversions were maintained below 5% to ensure differential conditions. Additional details of the reactor setup can be found elsewhere [20].

Based on the inlet and outlet concentrations and assuming differential reactor conditions, the conversion, activity, selectivity and yield were calculated as follows:

$$\text{Conversion (\%)} = (n_c/n_f) \times 100$$
$$\text{Activity (mol } C_3H_8 \text{ converted/g.s)} = F_{A0}X_A$$
$$\text{Selectivity (\%)} = (n_{hc}/n_c) \times (N_{hc}/N_p) \times 100$$
$$\text{Yield (\%)} = (n_{hc}/n_f) \times (N_{hc}/N_p) \times 100$$

where n_c and n_f are the number of moles of propane consumed and propane fed, respectively, n_{hc} is the number of moles of products (*e.g.*, propene, ethene, carbon oxides, etc.) formed, N_{hc} and N_p are the number of carbon atoms present in the products formed and propane, respectively, F_{A0} is the moles of propane fed per second and X_A is the conversion of propane per gram of the catalyst.

Blank reactor runs were conducted and no significant conversions were observed under the experimental conditions. For each catalyst several runs were performed and the average value is reported.

3. Results

The 5% Cr_2O_3 on Al_2O_3, CrAl, and 1% Cr_2O_3 on TiO_2, CrTi, catalysts were prepared and modified with oxides of Na, V and Mo. The sample nomenclature and the wt% composition are given in the first and second columns of tables 1 and 2. The third and fourth columns give the surface area and Raman shift and are discussed later.

3.1. Surface area

The surface areas of the Al_2O_3 support, CrAl and modified CrAl samples are shown in the third column of table 1. The third column of table 1 reveals that an initial decrease in surface area is observed for the CrAl samples. Further addition of Na, V and Mo oxides to CrAl samples decreases the surface area to a lesser extent. Detailed studies reported elsewhere reveal that Na_2O loadings up to 0.7 wt% do not significantly affect the surface area of the Na_xCrAl samples [30].

Table 1
Composition, surface area (S.A.) and Raman band positions for the CrAl and modified CrAl samples

Sample	Wt% M_xO_y	S.A. (m^2/g)	Raman shift (cm^{-1})
Al_2O_3	—	201	—
CrAl	5% Cr_2O_3	189	890
$Na_{0.06}CrAl$	0.3% Na_2O, 5% Cr_2O_3	179	890
VCrAl	8.8% V_2O_5, 5% Cr_2O_3	163	890, 805, 940
MoCrAl	9.1% MoO_3, 4.5% Cr_2O_3	169	850, 950

The surface areas of the TiO_2 support, CrTi and modified CrTi samples are shown in the third column of table 2. It is observed that the surface areas were relatively constant for modified and unmodified CrTi samples, but were lower than those for the pure support. The initial decrease in surface area of alumina and titania support may be due to the initial plugging of pores, as suggested previously [15,16,30–32]. Interestingly, when chromium oxide is deposited on alumina or titania it gains stability against further decreases in surface area when these samples are modified. Similar results have been reported for vanadium oxide modified Cr_2O_3/ZrO_2 catalysts [33].

3.2. XRD and Raman studies

XRD and Raman studies of the prepared samples were performed and for brevity the figures are not shown. The XRD pattern reveals the presence of peaks corresponding to the supports (γ-Al_2O_3 or anatase + rutile TiO_2). Raman studies under ambient conditions reveal that the spectra of the prepared

Table 2
Composition, surface area (S.A.) and Raman band positions for the CrTi and modified CrTi samples

Samples	Wt% M_xO_y	S.A. (m^2/g)	Raman shift (cm^{-1})
TiO_2	—	60	—
CrTi	1% Cr_2O_3	41	850
$Na_{0.06}CrTi$	0.06% Na_2O, 1% Cr_2O_3	43	850
VCrTi	1.8% V_2O_5, 1% Cr_2O_5	40	850, 940
MoCrTi	1.96% MoO_3, 0.98% Cr_2O_3	43	791, 842, 945

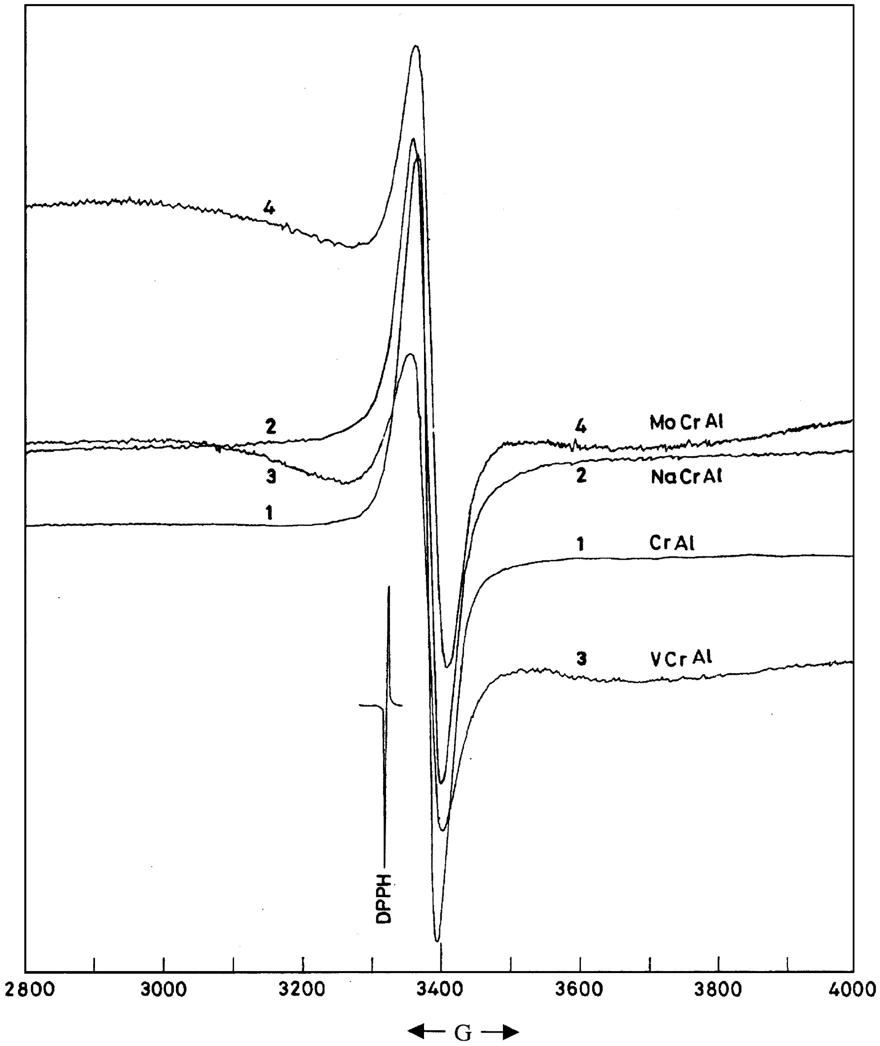

Figure 1. EPR spectra of CrAl and modified CrAl samples.

samples do not contain any sharp crystal features. Instead, Raman features corresponding to surface chromium, vanadium and molybdenum oxide species were observed in the 200–1100 cm^{-1} region. The Raman peak positions in the high wavenumber region (700–1100 cm^{-1}) for the modified and unmodified CrAl and CrTi samples are shown in the fourth column of tables 1 and 2, respectively. The peak corresponding to the Cr–O stretching mode (840–890 cm^{-1}) was present in all the modified and unmodified samples. For Na$_{0.06}$CrAl samples, only the surface chromia peaks (~890, 340 cm^{-1}) were detected. For the VCrAl and VCrTi samples an additional peak at ~805 and ~940 cm^{-1}, respectively, was observed in addition to the Cr–O stretching bond at ~890 cm^{-1}. The additional peak corresponds to the surface vanadium oxide species in the VCrAl and VCrTi samples [34]. Similarly, for the MoCrAl and MoCrTi samples an additional peak at ~950 cm^{-1} was observed, which corresponds to the surface molybdenum oxide species [35].

3.3. EPR

The EPR spectra obtained under ambient conditions for modified and unmodified CrAl and CrTi samples are shown in figures 1 and 2, respectively. The presence of a strong axially symmetric peak centered at ~3400 G was detected for unmodified and modified samples, and is due to the Cr^{5+} γ signal [36,37]. The g-value and ΔH ($g = 1.97$, $\Delta H = 40$–60 G) reveal that this peak is the same in all the samples. Moreover, the addition of vanadium or molybdenum oxide to the CrAl samples results in the formation of a broad peak ($\Delta H = 800$ G) in addition to the Cr^{5+} γ signal. This broad peak has been assigned to a dispersed Cr^{3+} β species [16,37]. The second broad peak corresponding to the Cr^{3+} β species that appears in the VCrAl and MoCrAl samples are, however, absent for the VCrTi and MoCrTi samples. Peaks corresponding to V^{4+} are absent in the spectra of the VCrTi and VCrAl samples.

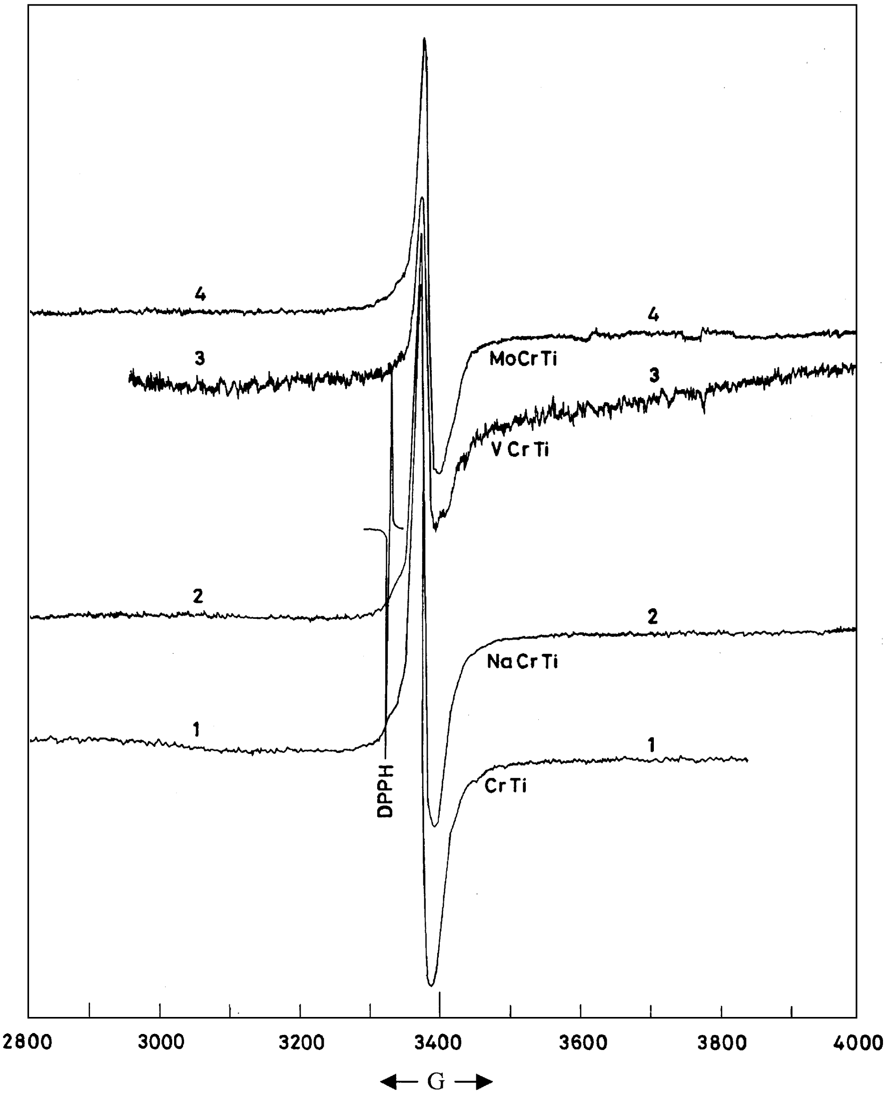

Figure 2. EPR spectra of CrTi and modified CrTi samples.

The intensities of the Cr^{5+} γ signal for the unmodified and modified CrAl samples are shown in figure 3. From figure 3 it is observed that the intensity of this peak decreases for CrAl samples when modified with vanadium and molybdenum but remains the same for the $Na_{0.06}$CrAl samples. Detailed studies reported elsewhere reveal that for Na_2O loadings up to 0.7 wt% no change in the intensity of the Cr^{5+} γ signal is observed [30]. Similarly to CrAl samples the Cr^{5+} γ signal intensity was observed to decrease for the CrTi samples modified with vanadium and molybdenum and to remain unchanged for the $Na_{0.6}$CrTi sample.

3.4. TPR

The TPR profiles for unmodified and modified CrAl samples are shown in figure 4. It is observed from figure 4 that for the CrAl samples modified with sodium oxide there is only one reduction peak with the $T_{max} \approx 663$ K. For the VCrAl and MoCrAl samples a reduction peak at ~659 K is observed along with a second peak at ~763 K for the VCrAl and at ~761 K for the MoCrAl samples. For the $Na_{0.6}$CrAl sample T_{max} was slightly shifted toward temperatures higher than that of the unmodified CrAl sample. A detailed TPR analysis of Na_xCrAl samples was performed. The T_{max} values and H/Cr ratios for the Na_xCrAl samples with different Na/Cr ratios are given in the second and third columns of table 3. The fourth and fifth columns in table 3 are data for the ODH of propane and are discussed later. From the second column of table 3 it is observed that T_{max} increased with increase in Na/Cr ratio. The H/Cr ratio given in the third column decreased with increase in Na/Cr ratio.

The TPR profiles for unmodified and modified CrTi samples are presented in figure 5. It is observed that the sodium modified CrTi samples possess a single T_{max} at ~633 K. However, two T_{max} values were

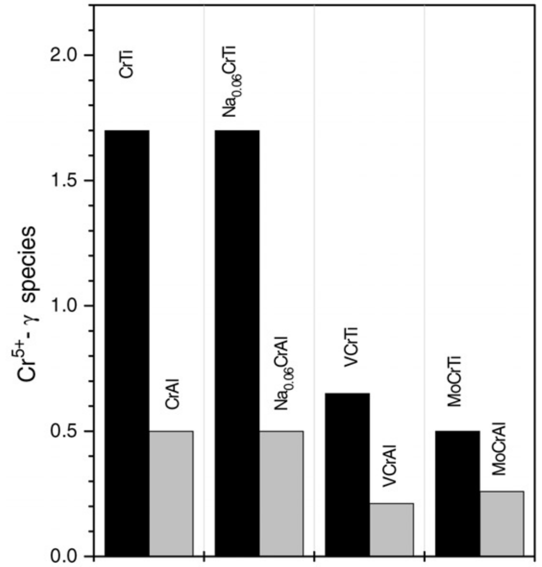

Figure 3. The Cr^{5+} γ signal intensity for unmodified and modified CrAl and CrTi samples. Signal has been normalized per mole of Cr.

observed for the VCrTi and MoCrTi samples. For VCrTi samples the reduction peaks were observed at ~641 and ~733 K, and for MoCrTi samples at ~633 and 741 K.

3.5. ODH of propane

ODH reactions of propane were performed for unmodified and modified CrAl and CrTi catalysts.

Table 3
TPR data, activity and selectivity for ODH of propane over sodium modified supported chromium oxide catalysts

Sample	T_{max} (K)	H/Cr	Activity × 10^6 [a] (mol/g s)	Selectivity [a] (%)
Na_0CrAl	663	1.9	2.40	70
$Na_{0.02}$CrAl	669	1.7	2.10	64
$Na_{0.06}$CrAl	668	1.2	1.60	60
$Na_{0.1}$CrAl	677	n.d	1.42	58
$Na_{0.15}$CrAl	684	n.d	1.12	50
Na_0CrTi	633	2.1	3.43	65
$Na_{0.06}$CrTi	639	1.6	1.72	51

[a] At 450 °C for a 3 : 1 propane to oxygen ratio.

Pure supports do not possess any activity for ODH of propane under the present operating conditions. Furthermore, the activities of MoO_3/Al_2O_3 and MoO_3/TiO_2 samples were observed to be negligible up to 723 K with the present setup.

The conversions of unmodified and modified CrAl and CrTi catalysts at temperatures ranging from 653 to 723 K are shown in figures 6 and 7, respectively. From figure 6 it is observed that the conversions of $Na_{0.06}$CrAl, and MoCrAl samples are less than that of the CrAl sample at all temperatures, the propane conversion being the lowest for the $Na_{0.06}$CrAl sample. However, the VCrAl sample shows a significant increase in propane conversion. The increase in conversion is more pronounced at higher temperature (723 K) for the VCrAl samples. Similarly, from figure 7 it is observed

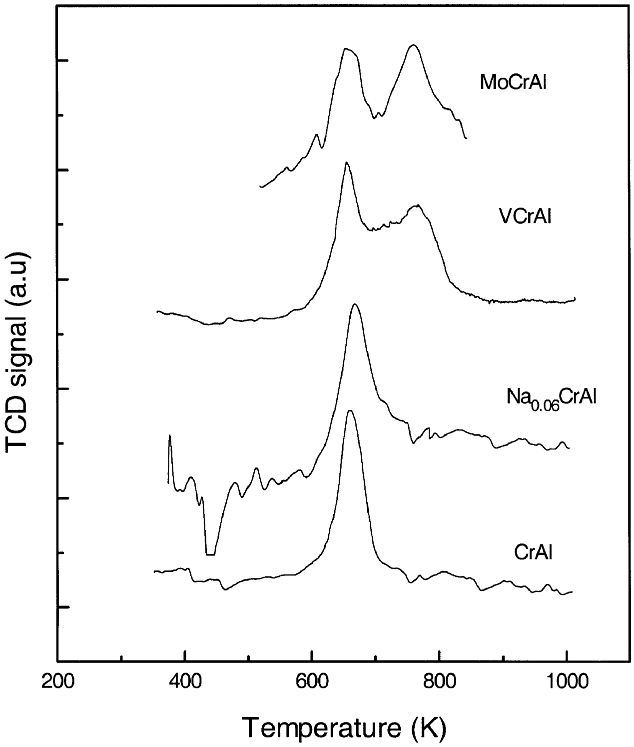

Figure 4. TPR profile for CrAl and modified CrAl samples: 10% H_2/He; ramp rate 10 °C /min.

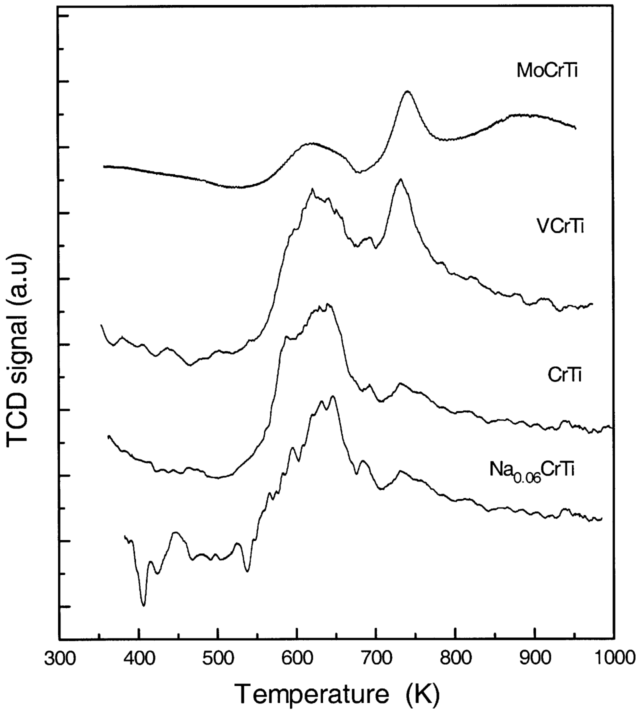

Figure 5. TPR profile for CrTi and modified CrTi samples. 10% H_2/He; ramp rate 10 °C /min.

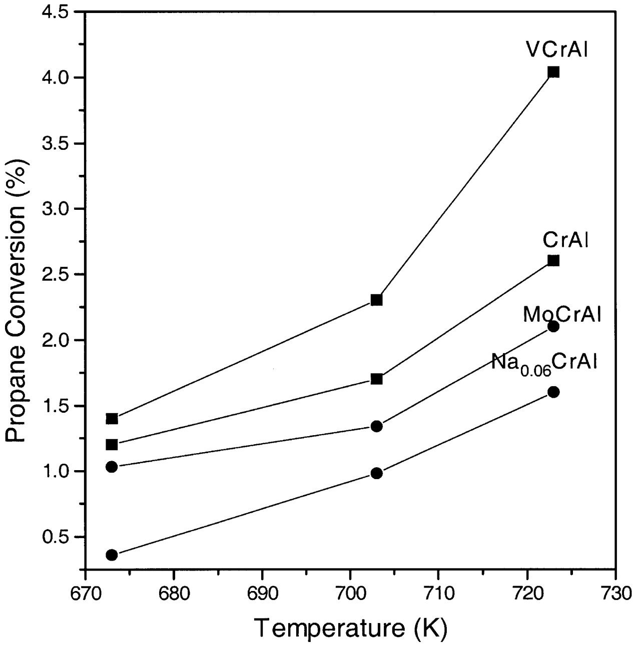

Figure 6. Propane conversion *versus* temperature for CrAl and modified CrAl ($Na_{0.06}CrAl$, VCrAl and MoCrAl) samples. $C_3H_8/O_2 = 3:1$; mass of the catalyst = 0.1 g, flow rate = 42.5 sccm.

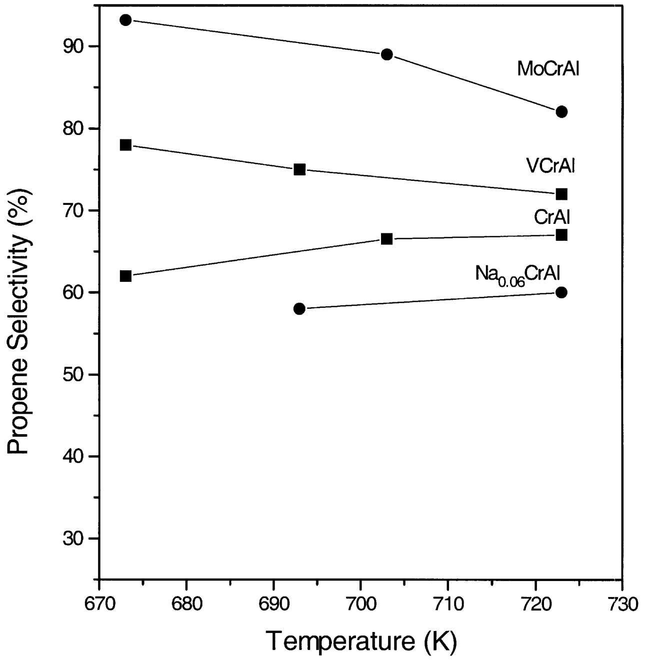

Figure 8. Propene selectivity *versus* temperature for CrAl and modified CrAl ($Na_{0.06}CrAl$, VCrAl and MoCrAl) samples. Experimental conditions as in figure 6.

that the conversions of $Na_{0.06}CrTi$ and MoCrTi samples are lower than that of the unmodified CrTi sample. Again, the propane conversion is the lowest for the $Na_{0.06}CrTi$ sample at all temperatures. Furthermore, the difference between the MoCrTi and CrTi samples is less than that for the MoCrAl and CrAl samples. The conversion of the VCrTi sample was significantly higher than that of CrTi samples at all temperatures.

The propene selectivity data for temperatures ranging from 653 to 723 K for modified CrAl and CrTi samples are shown in figures 8 and 9, respectively. It is observed from figure 8 that the selectivities for MoCrAl and

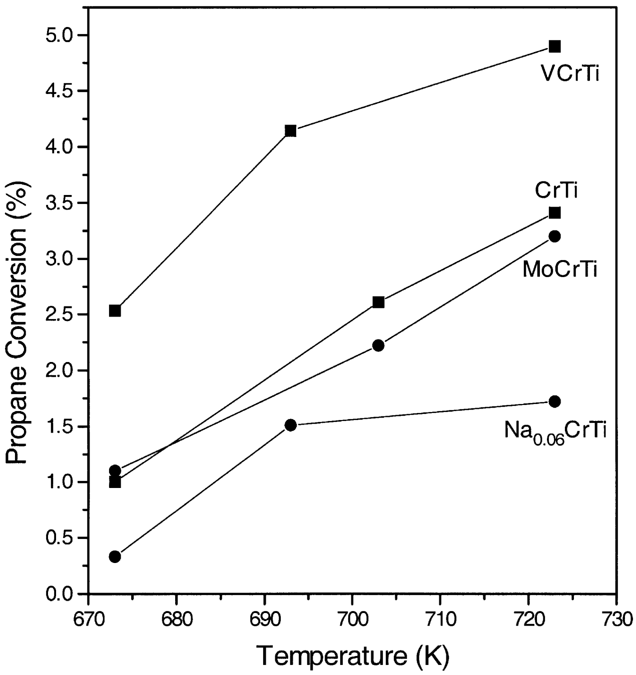

Figure 7. Propane conversion *versus* temperature for CrTi and modified CrTi ($Na_{0.06}CrTi$, VCrTi and MoCrTi) samples. Experimental conditions as in figure 6.

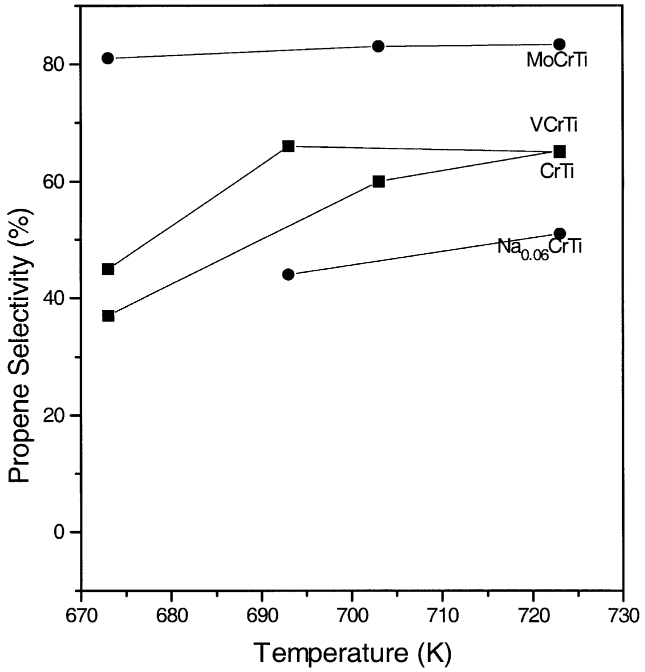

Figure 9. Propene selectivity *versus* temperature for CrTi and modified CrTi ($Na_{0.06}CrTi$, VCrTi and MoCrTi) samples. Experimental conditions as in figure 6.

Table 4

Yield for ODH of propane over modified CrAl and CrTi samples at different temperatures

T (K)	Yield (%)							
	CrAl	MoCrAl	VCrAl	$Na_{0.06}CrAl$	CrTi	MoCrTi	VCrTi	$Na_{0.06}CrTi$
673	0.81	0.96	1.10	0.12	0.35	0.97	1.12	0
703	1.13	1.20	2.14	0.82	1.56	1.83	2.89	0.73
723	1.74	1.72	2.87	1.20	2.27	2.90	3.20	0.87

VCrAl samples are higher than those for the CrAl samples at all temperatures. However, the propane selectivity decreased slightly for the MoCrAl and VCrAl samples with increase in temperature. For the NaCrAl samples the selectivity is lower than that for the unmodified CrAl samples at all temperatures. Similarly, figure 9 shows that the propane selectivity for MoCrTi and VCrTi samples is higher than that for the CrTi sample at all temperatures. Furthermore, the selectivity shows a slight decrease with respect to the temperature for the VCrTi sample and remains constant for the MoCrTi samples. The propane selectivity for $Na_{0.06}CrTi$ was lower than that for the CrTi samples at all temperatures.

To bring out the differences between the modified and unmodified CrAl and CrTi catalysts in detail, the numerical values of the propene yields for the ODH of propane at temperatures ranging from 673 to 723 K are presented in table 4. It is observed that the propene yields are higher for molybdenum and vanadium oxide modified CrAl and CrTi samples than that for unmodified CrAl and CrTi catalysts at all temperatures. For sodium modified CrAl and CrTi samples, however, the yield was lower than that for the unmodified catalysts.

4. Discussion

Supported chromium oxide catalysts possess surface chromium oxide species below monolayer coverages. Above monolayer coverages crystals of Cr_2O_3 are formed in addition to the surface chromium oxide species. These surface chromium oxide species are present as monochromates and polychromates [38]. Crystals of Cr_2O_3 are readily detected by Raman spectroscopy. The ratio of monochromates to polychromates is independent of the loading but appears to depend on the oxide support [39]. Interestingly, the ratio of isolated to polymeric surface vanadium and molybdenum oxides depends on the loading [7,34,40]. The monolayer limit for chromium oxide supported on the Al_2O_3 and TiO_2 supports used in the present study are ~12 and ~4 wt% Cr_2O_3, respectively [16].

In the present study, the supported chromium oxides were modified with different additives. The amount of modifiers was determined so that the coverage of chromium oxide and the chosen modifier did not exceed monolayer coverages. It was observed that the surface areas for the modified and unmodified CrAl and CrTi catalysts remain relatively constant. Thus, it appears that supported chromium oxide catalysts possess stability against any structural deformation or sintering by the introduction of the modifiers. XRD and Raman studies revealed that crystals of Cr_2O_3, V_2O_5, MoO_3 or Na–chromium oxide compounds were absent in the modified supported chromium oxide samples. Raman spectroscopy under ambient conditions detected the presence of surface chromium oxide species in all the samples. Furthermore, surface vanadium oxide in VCrAl and VCrTi samples and surface molybdenum oxide in MoCrAl and MoCrTi samples were observed by Raman spectroscopy under ambient conditions. Hence in the modified and unmodified CrAl and CrTi catalysts only surface metal oxide species were present.

The predominant oxidation states of chromium in CrAl and CrTi catalysts are Cr^{6+}, Cr^{5+} and Cr^{3+} [41]. Among these different oxidation states the paramagnetic Cr^{5+} and Cr^{3+} are readily detected by EPR spectroscopy. The EPR data revealed that the Cr^{5+} γ signal is present in both unmodified and modified supported chromium oxide catalysts. It was also observed that the intensity of the Cr^{5+} γ signal decreased for the VCrAl, MoCrAl, VCrTi and MoCrTi catalysts and remained constant for the NaCrAl and NaCrTi catalysts. Previous studies on a series of Cr_2O_3/Al_2O_3 and Cr_2O_3/TiO_2 samples revealed that the Cr^{5+} γ signal decreases as the Cr_2O_3 loading is increased [16]. It appears that in the present study a similar phenomenon occurs for the vanadium and molybdenum oxide modified CrAl and CrTi samples since the intensity of the Cr^{5+} γ signal also decreases. The Cr^{5+} γ signal is also present in the Na_xCrAl and $Na_{0.06}CrTi$ samples. Furthermore, the intensity of the Cr^{5+} γ signal does not change. In addition to the Cr^{5+} γ signal, the presence of a broad peak due to the Cr^{3+} β signal was also observed for VCrAl and MoCrAl samples. The Cr^{3+} β signal has been previously assigned to the presence of Cr_2O_3 crystals [36]. However, Raman spectral studies did not detect any crystals. This additional broad peak is also absent in the case of CrTi modified samples. Based on IR and Raman spectroscopic studies, Vuurman *et al.* [42] reported that owing to the introduction of a second metal oxide (*e.g.*

MoO_3, WO_3) the concentration of polymerized surface vanadium oxide species increased. In the present study it appears that owing to the introduction of vanadium and molybdenum oxide to the CrAl sample the local environment of chromium oxide sites is also affected, giving rise to the Cr^{3+} β signal. However, the reason why the development of the Cr^{3+} β signal is not observed for the CrTi modified samples is not clear. The difference may be due to the higher surface coverage of chromium oxide on the Al_2O_3 support. Furthermore, the assignment of the broad peak to Cr_2O_3 crystals appears to be inconsistent with the Raman studies since no crystal features are detected.

The TPR profiles for the modified and unmodified catalysts show the effect of additives on the reducibility of the surface chromium oxide species. For vanadium and molybdenum oxide modified CrAl samples two reduction peaks are observed. Comparing the T_{max} values with those of unpromoted CrAl, VAl, and MoAl samples revealed that the reduction peak at $\sim$660 K corresponds to surface chromium oxide species [15], and the reduction peak at $\sim$763 or $\sim$761 K corresponds to surface vanadium or molybdenum oxide species, respectively [32,43–45]. Similarly, CrTi catalysts modified with molybdenum and vanadium oxide also shows two reduction peaks, which are identified as being due to surface chromium oxide species (633–641 K) [16], surface molybdenum (741 K) or vanadium oxide species (733 K), respectively [22,46]. It appears that the vanadium and molybdenum oxide species do not influence the reduction characteristics of the surface chromium oxide species. No changes in reduction characteristics of the surface chromium oxide species are expected since vanadium and molybdenum oxide species are non-interacting modifiers [28]. The Na_2O modified CrAl and CrTi catalysts, however, show an increase in the T_{max} values as the Na_2O loading is increased. Furthermore, the H/Cr ratio decreases with increase in Na_2O loading. As expected for interacting modifiers, the reduction characteristics of the surface chromium oxide species are affected [34]. Thus, the surface chromium, vanadium and molybdenum oxide species retain their individual reducibility, whereas modifying the CrAl and CrTi samples with Na_2O results in a noticeable change in the reduction characteristics of the surface chromium oxide species.

The ODH reaction of propane provides an insight into the influence of the modifiers on the reactivity properties of supported chromium oxide catalysts. From previous studies it is observed that the activity of the CrAl and CrTi catalysts for ODH of propane increase with Cr_2O_3 loading until monolayer coverages and decrease with further increase in loading [16]. The propene selectivity also increases with loading owing to the decrease in exposed surfaces of the support [16]. In the present study, the ODH of propane over different Na_xCrAl catalysts and $Na_{0.06}$CrTi catalyst shows that there is a decrease in activity and propene selectivity. These changes are directly related to the decrease in reducibility observed in the TPR studies since the T_{max} temperature increased and the H/Cr ratio decreased. The decrease in ODH activity is not surprising since alkali metal ions are known to interact directly with surface metal oxide species in supported metal oxide catalysts [28,34]. This interaction poisons the surface chromium oxide, affecting the reduction characteristics and making it inactive for the ODH of propane. Since sodium interacts primarily with the surface chromium oxide sites the alumina support is still exposed to degrade any propene formed. The decrease in propene selectivity with addition of sodium suggests that additional alumina support is exposed, which is possible if the surface chromium oxide agglomerates. The interaction of sodium with the alumina support surface would decrease the acidity and the ability to degrade propene. Furthermore, comparison of data from EPR and ODH studies suggests that the paramagnetic Cr^{5+} species is not active for the ODH reaction since the Cr^{5+} γ signal is relatively constant but the propane conversion continuously decreases. Thus, the sodium modifier directly poisons the surface chromium oxide site, rendering it inactive for the ODH of propane.

A different type of behavior is observed for the molybdenum and vanadium oxide modified CrAl and CrTi samples. Addition of molybdenum oxide to the CrAl and CrTi catalysts results in a decrease in propane conversion and an increase in propene selectivity. A decrease in conversion of the MoCrAl and MoCrTi catalysts relative to the CrAl and CrTi catalysts is due to the decrease in the amount of redox chromium oxide species present in the same weight of sample. Indeed, normalizing the conversion data with respect to the amount of chromium oxide present results in the propane conversion being similar for the molybdenum modified and unmodified catalysts. The surface molybdenum oxide species is known to be a redox site, but is relatively inactive for propane ODH under the reaction conditions used in this study. At higher temperatures some ODH activity is, however, observed over supported molybdenum oxide catalysts. The surface molybdenum oxide species, being a non-interacting additive, covers the surface of the oxide supports. Consequently, the exposed Al_2O_3 and TiO_2 surface that were present in the CrAl and CrTi catalysts are unable to degrade propene formed by the surface chromium oxide species. Hence the propene selectivity increases for the molybdenum oxide modified catalysts.

With vanadium oxide addition to the supported chromium oxide catalysts, an increase in ODH activity is observed. This increase in ODH activity is directly related to the presence of an additional redox site, namely surface vanadium and chromium oxide sites. Furthermore, an increase in propene selectivity is observed for the VCrAl sample, but the increase in selectivity is not as pronounced as for the MoCrAl catalysts.

The propene selectivity is relatively constant for the VCrTi samples. In both cases the surface chromium and vanadium oxide sites cover the exposed Al_2O_3 or TiO_2 sites. Consequently, the exposed sites will not degrade propene to carbon oxides. The surface vanadium oxide site on Al_2O_3 has a high selectivity (~80%), whereas on TiO_2 the selectivity is lower (~60%). Hence it appears that the inherent selectivity of the surface vanadium oxide site is reflected in the overall selectivity of the VCrAl and the VCrTi catalysts [47].

In summary, the three modifiers used in the present study can be classified as interacting or non-interacting. The interacting modifier, sodium, directly coordinates with the surface chromium oxide species and affects the reducibility and propane conversion and propene selectivity. The non-interacting modifiers are of two types. Modifying the supported chromium oxide catalysts with vanadium oxide species results in the formation of additional redox sites that are also active for the ODH of propane. Modifying the supported chromium oxide catalysts with molybdenum results in a different behavior. The surface molybdenum oxide species is inactive under the present conditions and only helps in increasing the selectivity by covering the exposed support surface, which would otherwise degrade propene. Thus, the effect of additives/modifiers on the ODH of propane, although a unimolecular reaction, requires a more detailed analysis of the reaction network and the nature of the redox sites.

5. Conclusion

Modified supported chromium oxide catalysts were prepared by adding sodium, vanadium and molybdenum oxides to chromium oxide supported on Al_2O_3 and TiO_2 supports. The catalysts were prepared so that the coverage of chromium oxide and the modifier is below monolayer coverages, which were confirmed by characterization techniques. Furthermore, the characterization studies revealed the presence of surface chromium, molybdenum and vanadium oxide species for molybdenum and vanadium oxide modified CrAl and CrTi catalysts. The Cr^{5+} species was present in all modified and unmodified CrAl and CrTi catalysts. The intensity of the Cr^{5+} γ signal decreases for vanadium and molybdenum oxide modified CrAl and CrTi catalysts, but remains constant for sodium modified catalysts. Correlating the ODH activity with the presence of Cr^{5+} in the sodium modified samples suggest that these species are inactive for the ODH of propane. The TPR studies revealed that the reducibility of the surface chromium oxide species is decreased for sodium modified supported chromium oxide catalysts, but for molybdenum and vanadium oxide modified supported chromium oxide catalysts the reducibility was unaffected. Furthermore, surface vanadium oxide and molybdenum oxide species retain their individual reducibility.

Correlating the characterization information with the propane ODH results reveals that poisoning of the active chromium oxide sites occurs with sodium; vanadium oxide provides an additional active site and consequently an increase in activity for both CrAl and CrTi catalysts is observed; for molybdenum oxide modified CrAl and CrTi catalysts the activity was relatively the same, but the propene selectivity increased significantly.

References

[1] H.H. Kung, Adv. Catal. 40 (1995) 1.

[2] J. Haber, in: *Handbook of Heterogeneous Catalysis*, eds. G. Ertl, H. Knozinger and J. Weitkamp (Wiley-VCH, Weinheim, 1997), vol. 1, p. 792.

[3] T. Blasco and J.M. Lopez Nieto, Appl. Catal. A: Gen. 157 (1997) 117.

[4] E.A. Mamedov and V.C. Corberan, Appl. Catal. A: Gen. 127 (1995) 1.

[5] T.C. Watling, G. Deo, K. Seshan, I.E. Wachs and J.A. Lercher, Catal. Today 28 (1996) 139.

[6] A. Khodakov, J. Yang, S. Su, E. Iglesia and A.T. Bell, J. Catal. 177 (1998) 343.

[7] K.D. Chen, S. Xie, E. Iglesia and A.T. Bell, J. Catal. 189 (2000) 421.

[8] K.D. Chen, A.T. Bell and E. Iglesia, J. Phys. Chem. 104 (2000) 1292.

[9] R. Grabowski, B. Grzybowska, J. Stoczynki and K. Wcislo, Appl. Catal. A: Gen. 144 (1996) 335.

[10] M. Hoang, J.F. Mathew and K.C. Pratl, React. Kinet. Catal. Lett. 61 (1997) 21.

[11] P. Moriceau, B. Grzybowska, Y. Barbaux, G. Wrobel and G. Heequet, Appl. Catal. 168 (1998) 269.

[12] B. Grzybowska, J. Sloczynki, R. Grabowski, K. Wcislo, A. Kozlowska, J. Stock and J. Zielinski, J. Catal. 178 (1998) 687.

[13] D.W. Flick and M.C. Huff, Appl. Catal. A: Gen. 187 (1999) 13.

[14] S.M. Al-Zahrani, N.O. Elbashir, A.E. Abasaeed, and M. Abdulwahed, Ind. Eng. Chem. Res. 40 (2001) 781.

[15] M. Cherian, M.S. Rao, W.T. Wang, J.M. Jehng, A.M. Hirt and G. Deo, Appl. Catal. A: Gen. 233 (2002) 21.

[16] M. Cherian, M.S. Rao, A.M. Hirt, I.E. Wachs and G. Deo, J. Catal. 210 (2002) in press.

[17] I.E. Wachs, J.M. Jehng, G. Deo, B.M. Weckhuysen, V.V. Guliants, J.B. Benzigar and S. Sundaresan, J. Catal. 170 (1997) 75.

[18] G. Busca, L. Lietti, G. Ramis and F. Berti, Appl. Catal. B: Envir. 18 (1998) 1.1

[19] P. Viparelli, P. Ciambelli, L. Lisi, G. Ruippolo, G. Russo and J.C. Volta, Appl. Catal. A: Gen. 184 (1999) 291.

[20] G. Matra, F. Arena, S. Coluccia, F. Frusteri and A. Paramalina, Catal. Today 63 (2000) 197.

[21] A.A. Lemonidou, L. Nalabndian and I.A. Vasalos, Catal. Today 61 (2000) 333.

[22] K. Kohler, J. Engweiler and A. Baiker, J. Mol. Catal. A: Chem., 162 (2000) 423.

[23] Ch. Fountzoula, H.K. Matralis, Ch. Papadopoulou, G.A. Vogiatzis and Ch. Kordulis, J. Catal. 184 (1999) 5.

[24] J. El-Idrissi, M. Kacimi and M. Ziyad, Catal. Lett. 56 (1998) 221.

[25] D.W. Flick and M.C. Huff, Appl. Catal. 187 (1999) 73.

[26] R. Grabowski, B. Grzybowska, J. Sloczynski and K. Wcislo, Appl. Catal. A: Gen. 144 (1996) 335.

[27] R.H.H. Smits, K. Seshan and J.R.H. Ross, ACS Symp. Ser. 523 (1993) 380.

[28] G. Deo and I.E. Wachs, J. Catal. 146 (1994) 335.

[29] M. Cherian, M.S. Rao, S.S. Manoharan, A. Pradan and G. Deo, Topics Catal. 18 (2002) 225.

[30] R. Gupta, M.Tech. Thesis, IIT Kanpur (2002).

[31] V. Amte, M.Tech. Thesis, IIT Kanpur (1998).

[32] M.E. Harlin, L.B. Backman, A.O.I. Krause and J.T. Jylha, J. Catal. 182 (1999) 300.

[33] A. Trunschke, D.L. Hoang, J. Radnik and H. Lieske, J. Catal. 191 (2000) 456.

[34] G. Deo, I.E. Wachs and J. Haber, Crit. Rev. Surf. Chem. 4 (1994) 141.

[35] M.A. Vuurman and I.E. Wachs, J. Phys. Chem. 96 (1992) 5008.

[36] B.M. Weckhuysen, I.E. Wachs and R.A. Schoonheydt, Chem. Rev. 96 (1996) 3327.

[37] S. Khadder-Zinc, A. Ghorbel and C. Naccache, J. Mol. Catal. 150 (1999) 223.

[38] M.A. Vuurman, D.J. Stufkens, A. Oskam, J.A. Moulijn and F. Kapteijn, J. Mol. Catal. 60 (1990) 83.

[39] M.A. Vuurman, I.E. Wachs, D.J. Stufkens and A. Oskam, J. Mol. Catal. 80 (1993) 209.

[40] A. Khodakov, B. Olthof, E. Iglesia and A.T. Bell, J. Catal. 181 (1999) 205.

[41] M.I. Zaki, M.A. Hasan and N.E. Fouad, Appl. Catal. A: Gen. 171 (1998) 315.

[42] M.A. Vuurman, I.E. Wachs, D.J. Stufken, A. Oskam, G. Geo and I.E. Wachs, J. Chem. Soc., Farad. Trans. 92 (1996) 3259.

[43] M.C. Abello, M.F. Gomez and O. Ferretti, Appl. Catal. A: Gen. 207 (2001) 421.

[44] M.E. Harlin, V.M. Niemi and A.O.I. Krause, J. Catal. 195 (2000) 67.

[45] J.G. Eon, R. Olier and J.C. Volta, J. Catal. 145 (1994) 318.

[46] G.T. Went, L.J. Leu and A.T. Bell, J. Catal. 34 (1992) 479.

[47] K.R.S.K. Reddy, M.Tech. Thesis, IIT Kanpur, India (2002).