# Catalysis by Manganese Oxide Monolayers Part 1: Alumina and Magnesia Supports

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Manganesc oxide deposited on alumina and magnesia by different preparation methods has been studied with respect to its surface structure and reactivity. The controlled deposition of mono-atomic layers is effected by a grafting reaction between surface hydroxyl groups and manganese ethoxide. Repeated grafting allows multiple layers to be built up in a controlled manner. The properties of these catalysts differ from those prepared by conventional wet impregnation techniques and mechanical mixing. Test reactions involving carbon monoxide oxidation and isopropanol decomposition reveal significant differences in the activity and selectivity of the catalysts prepared by grafting, impregnation and mechanical mixing. The manganese oxide grafted to alumina shows bulk-like properties after a full monolayer is built up. XPS studies show that the grafting reaction leads to continuous films of the manganete covering the entire surface with monolayer thickness, whereas impregnation most likely results in small crystallites which cover only part of the surface. The calcination temperature is an important parameter determining the oxidation state of the manganese and the crystallinity of the oxide. Ammonia and isopropanol temperature-programmed desorption indicates that the acid/base and redox properties of the catalysts are considerably modified by a strong interaction between the support and the overlayer.

# 1. Introduction

Catalytically active metals are usually highly dispersed on a support [1]. As noble metals are rather expensive, there is a strong incentive to maximize the utilization of these materials. By depositing them on supports, the number of active surface atoms relative to those in the bulk is increased. Besides the obvious savings in expensive materials, supported catalyst systems offer other advantages such as the ease of handling, suitability for use in fixed or fluidized bed reactors, and improved thermal stability. The support was initially viewed as an inert material which merely stabilizes the metal catalysts. Thorough investigations of supported catalyst systems lead to the identification of additional effects such as strong metal-support interaction (SMSI) [2, 3] and structure-sensitive reactions [4].

Whereas supported metal catalysts have attracted considerable research efforts since the beginning of industrial catalysis, supported metal oxides have only been intensively investigated over the past decade owing to their growing importance in numerous catalytic applications [5, 6]. Metal oxides are generally much cheaper than noble metals, so that there is far less incentive to save the material by high dispersion. However, it has been shown recently that metal oxides dispersed as monolayers on a support can have greatly differing activities from the bulk material [7]. The following causes can be identified for modification in the catalytic activity:

- the catalytically active metal oxide frequently has a different crystal structure from the support. In an epitactic layer, the overlayer is forced to assume the structure of the support. Thus, the metal atoms in this layer are in an unusual environment and this will influence their catalytic activity.
- (2) The lattice parameters of the active phase are different from those of the support. Therefore, even if both

crystallize in the same structure, the atoms in the overlayer will be subjected to some stress or strain. They are thus in a state of higher energy and therefore potentially higher catalytic activity.

(3) The chemical bond between the atoms in the overlayer and the support will change the electron density at the metal atoms compared to the situation found at the surface of the bulk oxide. This electronic effect will also influence the catalytic properties.

Once the parameters influencing the activity in a dispersed monolayer are thoroughly understood, it will be possible to tailor-make a catalyst which optimally fulfils the steric and electronic requirements for any given reaction. In the molecular design of supported metal oxide catalysts, the synthesis method, oxide support, catalyst composition, calcination temperature, location and structure of the surface metal oxide species, as well as its reactivity have to be specified [8]. Monolayer dispersion of the active phase has been achieved by several techniques: (1) spontaneous spreading on heating of a mechanical mixture (2) wet impregnation of the support followed by calcination and (3) specific adsorption [9, 10]. Most of the work reported so far deals with vanadia layers on various supports.

The aim of the present study is to prepare supported manganate catalysts by these three methods and to compare their catalytic behaviour. Thus, it should be determined whether different preparation methods lead to identical surface species, or whether the preparation influences the final structure. Catalysts with different loadings were prepared to study the change in specific activity as one goes from submonolayer coverage to thicker layers which should finally approach bulk properties. The influence of the support on the catalytic activity is also investigated. Results with two supports, alumina and magnesia, are reported here.

Manganese fulfils the requirements for a good catalyst: the element occurs in several stable oxidation states (+2,

+3, +4, +7). While there are at present no major chemical processes that use manganates as catalysts, there are many industrial applications of this compound [11, 12]: manganese dioxide is used as depolarizator in carbon/zinc batteries, for the catalytic decomposition of hydrogen peroxide, and for selective oxidation reactions in the synthesis of fine chemicals. A manganese/copper-mixed oxide (hopcalite) is the active component in gas mask filters against carbon monoxide; this compound catalyses the carbon monoxide oxidation already at sub-zero temperatures [13, 14]. Alkali-metal promoted cobalt-manganese and coppermanganese oxides have been found to be more active catalysts for the water-gas shift reaction than the commercial high temperature shift catalyst based on iron and chromium oxides [15]. Manganese-containing catalysts have initially been used for ammonia oxidation to nitric oxide until platinum metal was found to be a superior catalyst for this reaction. Renewed interest focuses on manganese oxides for the selective catalytic oxidation of ammonia to nitrogen [16]. Ammonia emission due to ammonia slip remains a problem in the selective catalytic reduction (SCR) of nitrogen oxides with ammonia. Catalytic ammonia oxidation in an additional scrubber will be able to reduce the amount of ammonia which is released into the atmosphere. Manganese oxides have also been studied as active phase for the SCR reaction at low temperature [17, 18].

# 2. Experimental

# 2.1 Preparation

The catalyst supports used were  $\gamma$ -alumina and magnesia (Merck). For mechanical mixtures, weighed amounts of the dry support and manganese dioxide (Merck) were ball-milled together for 30 min, and the mixtures were subsequently calcined at 500 °C. These catalysts are referred to as S-xM, where S indicates the support (AI = alumina, Mg = magnesia), x stands for the weight % loading with manganese dioxide and M for mechanical mixing. Thus, the code Al-6M identifies a catalyst prepared by mechanical mixing and subsequent calcination of alumina with 6 weight % of manganese dioxide.

Catalysts prepared by wet impregnation with manganese acetate solution are referred to as S-xI. The third method used for catalyst preparation is grafting of metal alkoxides. In this method, manganese alkoxide,  $[Mn(OR)_2]$ , reacts with a surface hydroxyl group of the support S to form an S-O-Mn(OR) bond. Because of this selective reaction, this technique will result in no more than monolayer (ML) coverage. During calcination, the organic residues burn off or pyrolyze, and surface hydroxyl groups are regenerated on the manganese. Thus, it is possible to repeat the sequence of grafting and calcination several times and to build up thicker layers in a controlled fashion. The grafted catalysts are referred to as S-xG, where x indicates the number of grafting reactions. The manganese ethoxide used in this study was prepared according to ref. [19]. The support

material was dried in vacuo at 400 °C. It is known from the literature [9] that at this temperature, adsorbed water is removed but most surface hydroxyl groups remain intact. The support was allowed to cool and kept under dry nitrogen. It was then suspended in dry ethanol. An amount of the manganese ethoxide solution, containing a slight excess of the ethoxide over the quantity calculated for a monolayer coverage of the given weight of support, was added. The mixture was stirred for 24 hours at room temperature in order to bring the grafting reaction to completion. The grafted catalyst was filtered off under careful exclusion of moisture, washed several times with dry ethanol to remove any unreacted ethoxide, and dried overnight at 110°C. The catalysts were then calcined in air at 500°C for 6 hours. Multiple layers were built up stepwise by repeating the sequence of grafting and calcination.

# 2.2 Catalysts Characterization

The catalysts were characterized by a variety of techniques. X-ray fluorescence (Link XR200) and inductively coupled plasma-atomic emission spectroscopy (Plasmascan 710) were used to determine the metal loading, powder xray diffraction (Philips PW 1729, Cu K<sub>a</sub> source) to determine crystalline phases, and N<sub>2</sub> adsorption by the single point BET method (Micromeritics Flowsorb 2300) for measuring the surface area. Surface concentrations and overlayer thickness were measured by x-ray photoelectron spectroscopy (VG-Escalab MkII, magnesium anode (MgK<sub>a</sub> – 1253.6 eV) operated at 12 kV and 10 mA; residual pressure inside the spectrometer 10<sup>-8</sup> mbar or lower). Pellets were pressed from the powdered samples and mounted onto the sample holder with double-sided adhesive tape.

Surface acidity and redox properties were evaluated by thermal desorption (TPD) of ammonia and isopropanol. Temperature-programmed reduction (TPR) was used to determine the oxidation state and ease of oxidation/reduction. The apparatus for TPD/TPR was home-built; the setup is described in [20].

The activity of the catalysts was tested in the microreactor described previously [20]. Two test reactions were studied - oxidation of carbon monoxide and the decomposition of isopropanol. A constant weight of the catalysts  $(\sim 200 \text{ mg})$  was placed in a quartz reactor and the steady state products of each reaction were analyzed by gas chromatography. The oxidation of carbon monoxide was carried out in a stoichiometric mixture of 8 ml/min carbon monoxide and 4 ml/min oxygen made up in helium to a total flow of 50 ml/min. The decomposition of isopropanol (Merck, A.R.) was performed by injecting isopropanol at a rate of 1.88 ml/h (=10 ml/min STP gas) from a syringe pump (Harvard Instruments) into a bed of guartz chips which was placed on top of the catalyst in the reactor. The evaporation of the isopropanol takes place in a flow of helium (20 ml/min). The products formed in the reaction, namely acetone, propene, and water, were separated by gas chromatography (Porapak T column, TCD).

#### 3. Results and Discussion

# 3.1 Manganese Loading and Surface Area

Whereas the manganese loading is known for the mechanically mixed and the impregnated catalysts, this is not the case for the grafted samples. Thus, it had to be verified that each grafting reaction led to an additional monolayer of manganese oxide,  $MnO_x$ , on the surface. The amount of manganese in the catalysts was determined by x-ray fluorescence (XRF) and inductively-coupled plasma-atomic emission spectroscopy (ICP-AES). These data are contained in Table 1 together with values for the surface area. It is found that the XRF results are generally slightly higher than the ICP values. This may be due to the fact that the manganate forms an overlayer which attenuates the x-ray fluorescence from the support. Fig. 1 shows the metal loading against the number of grafting steps. The data points lay on a straight line through the origin. This indicates that each grafting reaction adds the same number of manganese atoms to the catalyst. It is therefore assumed that the amount of manganese added by the grafting reactions is not limited by the number of surface hydroxyl groups but by the space requirements of the bulky Mn(OEt)<sub>2</sub> reagent. From the known surface area of the support and the amount of manganate loading, a space requirement of 0.28 nm<sup>2</sup> for each -O-MnOEt-group on the alumina surface is calculated. This value has to be compared with the area of 0.11 nm<sup>2</sup> per Mn atom on the cubic face of  $\beta$ -Mn<sub>2</sub>O<sub>3</sub> (bixbyite structure). For magnesia, a slightly lower space requirement of 0.22 nm<sup>2</sup> was observed. Thus, only about one-half of a monolayer can be deposited with each grafting step.



 $MnO_2$  content as determined from XRF and ICP versus number of grafting steps. Support: y-alumina

Table i

Manganese content and surface area of alumina-supported catalysts

Samples	Surface area [m²/g]	% MnO <sub>2</sub>		Coverage	Average
		ICP	XRF	<i>0</i> *	state@
Al <sub>2</sub> O <sub>3</sub>	89.3				
Al-1G	89.5	3.2	4.49	0.31	2.00
Al-2G	89.3	5.4	6.47	0.50	2.32
Al-3G	90.7	8.1	12.5	0.91	3.04
Al-4G	88.3	11.1	14.2	1.14	2.97
Al-5G	79.9	17.0	17.5	1.65	2.90
AI-31	85.9	3.02	4.31		2.37
Al-6.451	81.9	6.47	7.67		2.65
Al-10I	77.5	9.89	11.6		3.57
Al-201	66.3	19.6	22.2		2.96
Al-3M	82.7	3.04	3.42		
Al-6.45M	81.9	6.43	6.47		
Al-10M	78.5	10.3	11.7		
Al-30M	65.0	30.2	32.1		

@ after calcination at 500 °C in air

\* based on Eq. (1)

The surface area of the alumina catalysts did not change significantly during the grafting reactions (Table 1). In contrast, a decrease by 25% is noted as the manganese loading is increased in the impregnated samples. This decrease is expected for systems in which the coating fills some of the pores of the support. The reduction of surface area observed with mechanically mixed systems is explained by the much lower specific surface area of the added manganese dioxide. With magnesia, one finds a drastic decrease in surface area by 56 - 88% depending on the preparation method (Table 2). For the grafted catalysts, most of this decrease takes place during the first grafting/calcination cycle. A de-

Table 2

Manganese content and surface area of magnesia-supported catalysts

Samples	Surface area [m <sup>2</sup> /g]	% MnO <sub>2</sub>		Average
		ICP	XRF	state@
MgO	164.5			
Mg-1G	40.4	9.2	10.9	3.02
Mg-2G	51.7	12.2	14.0	3.22
Mg-3G	63.5	16.2	17.9	3.23
Mg-4G	68.0	16.4	20.8	3.36
Mg-5G	68.0	25.7	21.5	3.25
Mg-51	82.4	6.04	5.34	3.90
Mg-10I	85.4	10.0	9.50	4.00
Mg-12I	81.9	11.5	10.9	3.80
Mg-15I	102.5	14.1	12.4	3.54
Mg-20I	56.8	18.8	24.6	3.54
Mg-30I	23.8	28.2	35.7	3.68
Mg-40I	19.7	40.1	44.0	3.94
Mg-5M	50.0	5.17	4.22	
Mg-10M	35.5	9.58	9.36	
Mg-12M	31.9	11.3	12.0	
Mg-15M	36.8	15.1	13.7	

@ after calcination at 500 °C

crease in surface area of a similar magnitude has also been observed with the untreated magnesia after it was subjected to the same temperature treatment. Each grafting step involves an additional calcination step. It is therefore remarkable that the surface area increases again after the first manganate layer has been completed. This implies that the growth pattern of manganate on manganate is not in smooth layers. For the impregnated catalysts, the surface area drops by 50% with 5% manganate addition but is stabilized by larger additions and even appears to increase slightly for 15% loading. This may be due to the formation of a mixed spinel phase, Mg<sub>2</sub>MnO<sub>4</sub>, at the surface of the catalysts, which reduces the atom mobility. However, the existence of this phase could not be confirmed by XRD. Even higher amounts of manganese result in a decrease in surface area.

The oxidation state of the manganese in the overlayers was determined by temperature-programmed reduction. For the alumina-supported samples prepared by grafting and impregnation, the value lies between +2 and +3. This is supported by XRD results where in some cases with high loadings, the diffraction pattern of Mn<sub>2</sub>O<sub>3</sub> could be discerned. The magnesia-supported samples have somewhat higher manganese oxidation states. For the grafted samples, the manganese appears to be a mixture of manganese (+2) and manganese (+3) while for the impregnated samples, the oxidation state is higher, between +3 and +4. Mechanically mixed samples after calcination to T < 500 °C show diffraction peaks corresponding to manganese (+4) species on both magnesia and alumina.

#### 3.2 Effect of Calcination Temperature

The powder XRD spectra of two mechanically mixed samples, Al-6.45M and Al-30M, were studied as a function of calcination temperature (Fig. 2). y-alumina itself gives rise to only a few weak broad peaks owing to its amorphous state. After calcination at low temperature (T < 500 °C), MnO<sub>2</sub> could be identified by the peak at  $2\theta = 28^{\circ}$  (JCPDS 12-0716) whereas after calcination at higher temperatures, Mn<sub>2</sub>O<sub>3</sub> was formed as evidenced by the peak at 33° (JCPDS 18-0803). It was found that an intermediate temperature of 500 - 600 °C results in the smallest x-ray signal. Obviously in this temperature range, a phase change takes place which leads to the breaking up of the MnO<sub>2</sub> crystals but the new phase does not yet recrystallise into bigger particles. Thus, most of the crystallites are x-ray amorphous and the intensity of the diffraction lines is low. The formation of Mn<sub>2</sub>O<sub>3</sub> from MnO<sub>2</sub> has been reported to take place in air at 800°C or during heating in vacuo at 500°C [21]. In the present study, the samples were calcined at 500 °C as this temperature is sufficient to decompose the alkoxides and does not cause severe loss in surface area.

# 3.3 X-Ray Diffraction

For both grafted and impregnated alumina catalysts, no diffraction lines of any crystalline  $MnO_x$  phase were ob-

served for samples with low loadings. With higher loadings (Al-4G, Al-5G and Al-20I), a peak at  $2\theta = 33^{\circ}$  appeared, indicating the presence of Mn<sub>2</sub>O<sub>3</sub>. The absence of the other more intense diffraction lines of this species from the observed spectra may indicate that ordering in two dimensions takes place in the overlayer. The limited thickness in the third dimension prevents the occurrence of sufficiently sharp reflexes (hkl) with  $l \neq 0$ . In contrast, catalysts prepared by mechanical mixing and calcination at 500 °C show all of the more intense diffraction lines for MnO<sub>2</sub>.

Magnesia-supported samples prepared by either grafting or impregnation show only the diffraction signals of MgO. The manganate spreads obviously in a thin layer on or below the surface without forming any extended threedimensional crystallites. However,  $MnO_2$  was easily detected in all the mechanical mixtures, with 5% to 15% loading. Hence, it can be concluded that both the grafting





XRD of Al-6.45M and Al-30M as a function of calcination temperatures.  $\odot$  MnO\_2,  $\bullet$  Mn\_2O\_3

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and impregnation method result in thin x-ray amorphous layers of manganate, whereas mechanical mixing and subsequent heat treatment does not lead to spreading, but that in these systems, the crystalline identity of the manganate is maintained.

# 3.4 X-Ray Photoelectron Spectroscopy

XPS is a surface sensitive technique. It is therefore well suited to examine the surface composition. The mean free path of photoelectrons in a condensed phase is limited to a few nm before they are inelastically scattered and lose energy. Depending on their kinetic energy, only photoelectrons which originate from the topmost 4-5 atomic layers contribute significantly to the detected signal. Therefore, if the manganate forms layers which completely cover the surface, one will observe a considerable attenuation of the support signal once more than one layer has formed. On the other hand, if the deposit covers only parts of the surface in correspondingly thicker layers, then the support signal will initially decrease with increasing manganate loading, but later reach a constant value [22]. In Fig. 3, the ratio of the photoelectron signal  $I_{\rm Mn}/I_{\rm Al}$  is plotted against the manganate loading. Grafted and impregnated catalysts



Fig. 3

Photoelectron intensity  $I_{Mn}/I_{Al}$  versus % MnO<sub>2</sub> for grafted, impregnated and mechanically mixed catalysts. Support:  $\gamma$ -alumina, (...) calculated  $I_{Mn}/I_{Al}$  for impregnated and grafted catalysts based on Eqs. (2) and (3) respectively

show drastically different behaviour: in the case of the grafted catalysts, the ratio  $I_{Mn}/I_{Al}$  increases sharply with manganate loading, whereas for the impregnated and mechanically samples, this quantity increases much more slowly. Similar results were obtained with the magnesia-supported catalysts.

The photoelectron signal can be calculated for two different cases: (1) the deposition is in patches or islands of thickness N atomic layers, and (b) the surface is covered layer by layer. The first case has been considered by Inumaru et al. [10]. The overlayers are assumed to consist of  $Mn_2O_3$ . The alumina surface is partially covered with a manganate layer of thickness Nt, where N is the number of layers and t is the thickness of one atomic layer of  $Mn_2O_3$ . The coverage,  $\theta$ , is related to the loading w by Eq. (1):

$$\theta = w/(SAN) \quad , \tag{1}$$

where

 $S = \text{surface area } (\text{m}^2/\text{g})$  $A = \text{weight of an ideal } \text{Mn}_2\text{O}_3 \text{ monolayer} =$ 

 $1.4112 \times 10^{-3}$ g/m<sup>2</sup>.

The inelastic mean free path (IMFP) of Al 2p photoelectrons in the Mn<sub>2</sub>O<sub>3</sub> overlayer is  $\lambda_{AIMn}$ . The number of Al photoelectrons is reduced by a factor of exp  $(-Nt/\lambda_{AIMn})$  by passing through the Mn<sub>2</sub>O<sub>3</sub> layer. Likewise,  $\lambda_{MnMn}$  is the inelastic mean free path of Mn 2p photoelectrons in a Mn<sub>2</sub>O<sub>3</sub> overlayer, and  $\lambda_{AIAI}$  the inelastic mean free path of Al 2p photoelectrons in bulk Al<sub>2</sub>O<sub>3</sub>. The XPS intensity ratio,  $I_{Mn}/I_{AI}$ , can be expressed by Eq. (2):

$$\frac{I(Mn)}{I(Al)} = \frac{\sigma_{Mn}\lambda_{MnMn}d_{Mn}\theta(1 - \exp(-Nt/\lambda_{MnMn}))}{\sigma_{Al}\lambda_{A|Al}d_{Al}(1 - \theta + \theta\exp(-Nt/\lambda_{AlMn}))} , \qquad (2)$$

where

$$\theta$$
 = coverage

 $\sigma_{Mn}$  = ionization cross section for Mn = 8.99 barns/C [23]

 $\sigma_{Al}$  = ionization cross section for Al = 0.5735 barns/C [23]

 $\lambda_{MnMn} = IMFP$  of Mn 2p photoelectron in Mn<sub>2</sub>O<sub>3</sub> = 0.962 nm [23]

 $\lambda_{AlAi}$  = IMFP of Al 2p photoelectron in Al<sub>2</sub>O<sub>3</sub> = 1.636 nm [24]

 $\lambda_{AlMn} = IMFP$  of Al 2p photoelectron in  $Mn_2O_3 = 1.574$  nm [24]

 $d_{\rm Mn}$  = number of Mn atoms in unit volume of Mn<sub>2</sub>O<sub>3</sub> = 34.42 nm<sup>-3</sup>

- $d_{Al}$  = number of Al atoms in unit volume of Al<sub>2</sub>O<sub>3</sub> = 44.91 nm<sup>-3</sup>
- t = thickness of ideal  $Mn_2O_3$  (111) monolayer = 0.3136 nm

N = number of layers.

In the event that the growth of the overlayer occurs layer by layer, the intensity ratio  $I_{Mn}/I_{A1}$  should follow Eq. (3):

$$\frac{I(\mathrm{Mn})}{I(\mathrm{Al})} = \frac{\sigma_{\mathrm{Mn}}\lambda_{\mathrm{MnMn}}d_{\mathrm{Mn}}[(1-\theta)(1-\exp\left(-(N-1)t/\lambda_{\mathrm{MnMn}}\right)) + \theta(1-\exp\left(-Nt/\lambda_{\mathrm{MnMn}}\right))]}{\sigma_{\mathrm{Al}}\lambda_{\mathrm{AlAl}}d_{\mathrm{Al}}\exp\left[-(N-1)t/\lambda_{\mathrm{AlMn}}\right](1-\theta+\theta\exp\left(-Nt/\lambda_{\mathrm{AlMn}}\right))}$$
(3)

The coverage  $\theta$  is now given as

$$\theta = \frac{w}{SA} - (N - 1) \quad , \tag{4}$$

where N is the number of layers and  $0 \le \theta \le 1$ .

The variation of the ratio  $I_{\rm Mn}/I_{\rm Al}$  with loading for the impregnated samples can be fitted with Eq. (2), where N = 12 - 16. This strongly suggests that by impregnation, crystallites of  $Mn_2O_3$  about 4-5 nm thick are deposited on the support. However, for the grafted samples, a good fit is obtained with Eq. (3) where only after the third grafting is a monolayer completed. The fourth grafting starts the formation of the second overlayer on top of the completed monolayer. Hence, from the variation of the XPS intensity ratio with manganate loading, it is possible to distinguish the way in which the manganate is deposited on the surface of the support.

#### 3.5 Acidity of Catalysts

The acidity of the catalyst surfaces was probed by temperature-programmed desorption of ammonia and of isopropanol. In Fig. 4, the desorption spectra after ammonia adsorption are shown for y-alumina, and the catalysts Al-2G and Al-6.45I. There are considerable differences in the shape of the ammonia desorption signal and in the reaction products formed. In all cases, the desorption of ammonia results in a broad asymmetric peak with a tail towards high temperatures. On  $\gamma$ -alumina,  $T_{max}$  is at 105 °C, but it moves to higher temperatures for the other two samples. The low temperature peak can be assigned to desorption from Brønsted sites according to findings by Nickl et al. [25]. Brønsted sites bind ammonia less strongly than the Lewis acid sites which account for the tail of the desorption signal towards temperatures higher than 200 °C. In addition, over  $\gamma$ -alumina a small amount of N<sub>2</sub>O is observed whereas the manganate-covered surfaces catalyze ammonia oxidation to  $N_2$ ,  $N_2O$  and NO. The formation of  $N_2$  over Al-6.45I is particularly interesting as it suggests that the surface structure of such a catalyst may be suited for selective ammonia oxidation to N<sub>2</sub> rather than to NO or N<sub>2</sub>O. Singoredjo et al. have studied the use of manganese oxides prepared by impregnation as active phase for the SCR of  $NO_x$  with ammonia at low temperature [17, 18]. In Table 3, the amount of ammonia (indicative of the total number of acidic sites) and the peak desorption temperature (indicative of the strength of the acidic sites) are given for the various alumina catalysts. Also contained in the Table is the amount of N<sub>2</sub>O formed together with its main desorption temperature. N<sub>2</sub>O desorbs in a broad peak from these catalysts. It seems that the number of acid sites increases initially with manganate loading and reaches a maximum at 6.45% (Al-6.45I and Al-2G). Whereas the number and strength of the acid sites on the surface of the grafted

and impregnated catalysts are comparable, there is a considerable difference in the amount of N<sub>2</sub>O formed. The selectivity towards N<sub>2</sub>O is increased as the number of grafted layers increases. Over impregnated catalysts, less  $N_2O$  is formed than over the grafted samples.



Fig. 4

Temperature-programmed desorption of NH<sub>3</sub> from Al<sub>2</sub>O<sub>3</sub>, and the catalysts Al-2G and Al-6.45I. Desorption signals are arbitrarily displaced on the intensity axis for clarity. Sample weight = 0.20 g

Table 3 Ammonia TPD of alumina-supported samples

Samples	Τ <sub>ΝΗ</sub> , [°C]	$NH_3 [\times 10^{12} molecules/cm^2]$	$T_{N_2O}$ [°C]	N <sub>2</sub> O [×10 <sup>12</sup> molecules/cm <sup>2</sup> ]
Al <sub>2</sub> O <sub>3</sub>	105	130		_
Al-1G	99	158	600	5.09
Al-2G	178	182	316	15.7
Al-3G	123	169	340	15.1
Al-4G	100	154	340	22.4
Al-5G	124	174	410	25.0
Al-3I	110	198	475	1.54
Al-6.45I	147	264	313	3.86
Al-10I	110	212	272	5.31
Al-20I	110	178	313	3.71

Magnesia does not adsorb any ammonia above room temperature. However, after grafting or impregnation with manganate, the acidity of the sample is increased. After ammonia adsorption, desorption of NH<sub>3</sub>, N<sub>2</sub>O, NO and N<sub>2</sub> is observed for both the grafted and impregnated catalysts. The number of acid sites on both types of catalysts are comparable, between  $5-9 \times 10^{13}$  molecules/cm<sup>2</sup>. However, the number of acidic sites on the magnesia-supported catalysts is 2-4 times smaller than on the alumina catalysts.

# 3.6 Isopropanol TPD

Selectivity in the decomposition of isopropanol is used for investigating the acid-base and redox properties of surfaces [26]. Dehydration of isopropanol to propene (Eq. 5) is assumed to be catalyzed by an acid site while the dehydrogenation to acetone (Eq. 6) is catalyzed by both acid and basic sites through a concerted mechanism.

 $CH_3 - CH(OH) - CH_3 \rightarrow CH_2 = CH - CH_3 + H_2O \qquad (5)$ 

$$CH_3 - CH(OH) - CH_3 \rightarrow CH_3 - C(O) - CH_3 + H_2$$
 (6)

Hence, the rate of dehydration is regarded as a measure of the acidity of the catalyst, while the ratio of the dehydrogenation rate to the dehydration rate is taken as a measure of the basicity [27]. In fact, the dehydrogenation reaction has been found to require an additional redox ability [28]. It has been observed previously that temperature-programmed desorption of isopropanol gives results which are different from steady-state isopropanol conversion [29, 30] over the same catalyst. Notably, in desorption measurements, more deep oxidation products are observed, which indicate the reduction of the catalyst surface. Also, acetone formation is commonly found even over acidic surfaces which give propene with high selectivity when the measurements are done under steady-state conditions.

It is well-known that alumina behaves as a Brønsted acid. In TPD, unreacted isopropanol desorbs at  $104^{\circ}$ C with a small shoulder at 250°C. Propene (Fig. 5a) also desorbs in two peaks, at  $104^{\circ}$ C (10%) and 308°C (90%). Acetone appears with peaks at 104°C and 303°C (Fig. 5b). MnO<sub>2</sub> on the other hand is a strong oxidizing agent. Therefore, isopropanol does not desorb intact from this surface. Instead, a very strong  $CO_2$  signal is found around 680 °C which probably indicates the decomposition of a surface carbonate.

Over the grafted catalysts, the following trends are observed as a function of the number of grafting reactions. Propene desorbs in two peaks, at  $\sim 100$  °C and at  $\sim 250$  °C (Fig. 5a). The high temperature propene peak decreases much more rapidly than the low temperature signal so that it has disappeared completely for Al-5G. On the other



Desorption spectra following isopropanol adsorption on grafted alumina samples: (a) propene, (b) acctone. Sample weight = 0.20 g

hand, the acetone signal increases with manganate content and is the main signal for Al-3G and Al-4G (Fig. 5b). The two peaks observed on alumina coalesce to form one main peak at an intermediate temperature of ~160 °C from Al-3G upwards. CO<sub>2</sub>, the product of deep oxidation, is also formed over these samples and desorbs above 300 °C. For Al-5G, CO<sub>2</sub> becomes the main desorbing species.

As with the grafted samples, the propene desorption signal from the impregnated samples also shows two peaks: one at  $\sim 100$  °C and a second at  $\sim 300$  °C (Fig. 6a). The



Fig. 6

Desorption spectra following isopropanol adsorption on impregnated alumina samples: (a) propene, (b) acetone. Sample weight = 0.20 g

propene signal diminishes with increasing manganate loading. The acetone signal has a different desorption profile compared with the grafted samples of similar manganate loading (Fig. 6b). The peaks are broader than those from the grafted catalysts. The acetone signal from Al-3I shows two incompletely resolved peaks, one at 136°C and another at ~ 300°C. The higher loading in Al-6.45I leads to a decrease of the low temperature peak, and the high temperature peak now appears at 320°C. At an even higher loading (Al-10I), the high temperature peak decreases likewise, and considerable amounts of CO and CO<sub>2</sub> are desorbed. Desorption spectra from mechanical mixtures resemble those from  $\gamma$ -alumina at low loadings, while at high loadings (>10%), the spectra look similar to the one from bulk MnO<sub>2</sub>.

Over the magnesia-supported catalysts, the desorption products after isopropanol adsorption are isopropanol, acetone, propene, CO<sub>2</sub>, and methane. These can be classified according to the surface reactions they represent: (i) reversible adsorption (isopropanol), (ii) dehydrogenation (acetone), (iii) dehydration (propene) and (iv) oxidative decomposition (CO<sub>2</sub>, methane). Propene desorbs from magnesia in two peaks, at 97 °C and 282 °C. However, grafted samples show only the low temperature peak. The acetone signal is more prominent than the propene peak for all samples. Over magnesia, one broad acetone peak was observed with the maximum at 94 °C. The maximum moves to higher temperatures as the manganate layers are built up. Unlike the grafted samples, the impregnated samples show double peaks for both the propene and acetone.

The different TPD spectra obtained for the various samples indicate that different surface structures resulted from the different preparation methods.

# 3.7 Activity Tests

In order to further confirm the hypothesis that epitactic growth modifies the catalytic behaviour of the manganese atoms relative to that on the surfaces of  $MnO_2$  or  $Mn_2O_3$ , we investigated the oxidation of carbon monoxide and the decomposition of isopropanol over these catalysts.

Table 4					
Ammonia	TPD o	of	magnesia-su	pported	samples

Sample	T <sub>NH3</sub> [°C]	$NH_3$ [×10 <sup>12</sup> molecules/cm <sup>2</sup> ]			
MgO					
Mg-1G	98	53.4			
Mg-2G 98		89.1			
Mg-3G	130	92.6			
Mg-4G	124	87.3			
Mg-5G	124	88.2			
Mg-5I	109	91.3			
Mg-10I	136	104			
Mg-12I	137	83.7			
Mg-15I	109	92.6			

#### 3.7.1 CO Oxidation

# Effect of Calcination Temperature

Fig. 7 compares the activity of several mechanically mixed samples of type Al-6.45M, which had been calcined at different temperatures. Samples calcined at 500 °C and below show very similar behavior. Calcination at 600 °C leads to increased activity as indicated by the lower take-off temperature of the reaction. Samples calcined at even higher temperatures ( $\geq$ 700 °C) have again less activity. This maximum in activity can be correlated with the structural information obtained from the XRD spectra. Samples calcined at 600 °C are almost x-ray amorphous, indicating that the crystallites are very small after the phase transformation  $2MnO_2 \rightarrow Mn_2O_3 + \frac{1}{2}O_2$ . Hence the calcination temperature can play a very important role in determining the catalytic activity.



Price 7 Percent CO conversion versus temperature for the catalyst Al-6.45M. Parameter is the calcination temperature. Sample weight = 0.20 g

#### Alumina-Supported Catalysts

In order to compare the activity of the different catalysts, the temperature  $T_{50}$  at which 50% conversion was attained is reported. The sample weight was held constant at 0.20 g. Fig. 8 shows the change of  $T_{50}$  with manganese loading for the samples prepared by grafting, impregnation and mechanical mixing. The mechanical mixtures behave simply as physical mixtures of the components; the activity is low



 $T_{50}^{\circ}$  for CO oxidation versus % MnO<sub>2</sub> loading for grafted, impregnated and mechanically mixed aluminia samples (see text for further details). Sample weight = 0.20 g

in the most dilute catalyst and increases with increasing molar fraction of MnO<sub>2</sub> towards the value for pure MnO<sub>2</sub> (285 °C). A very different behaviour is observed over the grafted catalysts. Here, the activity is comparable to that of bulk MnO<sub>2</sub> already at  $\theta \approx 1/2$  (Al-2G) and surpasses it for multiply grafted systems. The fact that the activity increases even after one full monolayer has been deposited indicates that the first layer has not yet the optimal conformation for an oxidation catalyst. A certain relaxation of the lattice stress induced by interaction with the support is needed for optimal catalytic activity. A similar trend is observed for the impregnated system, where already at 3% loading an activity comparable to that of bulk MnO<sub>2</sub> is attained. The activity increases up to 10% loading and remains little changed for higher loadings. At this point, the catalyst is considerably more active than bulk MnO<sub>2</sub>. This observation is in agreement with the model that the manganate islands on the impregnated catalysts are thicker than the layers on the grafted catalysts with comparable loading. Thus, less lattice strain exists in the outer catalytically active layer.

# Magnesia-Supported Catalysts

Magnesia itself shows some activity for CO oxidation. The addition of manganates by grafting increases the activity, but only at Mg-5G does the catalyst show an activity comparable to that of pure MnO<sub>2</sub> (Fig. 9). Impregnated systems show higher activities than the grafted catalysts and indeed surpass that of pure MnO<sub>2</sub> for >30% loading. The



 $T_{50}$  for CO oxidation versus % MnO<sub>2</sub> loading for grafted, impregnated and mechanically mixed magnesia samples. Sample weight = 0.20 g

higher activity of these heavily loaded catalysts may simply result from their higher surface areas  $(20 - 25 \text{ m}^2/\text{g})$  compared to bulk MnO<sub>2</sub>  $(3.76 \text{ m}^2/\text{g})$ .

#### 3.7.2 Isopropanol Decomposition

# Alumina-Supported Catalysts

Steady state measurements on isopropanol decomposition was carried out in the flow reactor. The only products observed are propene and acetone. Propene results from the dehydration of isopropanol while acetone is the product of dehydrogenation. Neither CO nor CO<sub>2</sub> were detected during these measurements. The catalysts became active between 250°C and 450°C. Pure alumina and the catalysts Al-1G and Al-2G show 100% selectivity towards propene, indicating that the acid sites dominate the reactivity (Fig. 10a). MnO<sub>2</sub> on the other hand catalyses acetone formation with close to 100% selectivity below 300°C, the selectivity decreasing to 90% as the temperature is raised. Multiply grafted catalysts (Al-3G and above) show increasing acetone formation at low temperatures. The change in selectivity towards propene at higher temperatures has been attributed to the difference in activation energy of the two competing reactions [26]. The activation energy of the dehydration reaction is generally higher than that of the dehydration reaction, so that at higher temperatures, propene formation dominates.

Impregnated catalysts have a higher selectivity towards acetone than the grafted catalysts (Fig. 10b). Al-3I has only 3% MnO<sub>2</sub> loading yet its selectivity is 70% acetone at

300 °C. This is very different from the  $\gamma$ -alumina support which constitutes 97% of the total mass. The selectivity towards acetone increases with manganate loading, but the catalysts with the highest loading (Al-10I and Al-20I) show very similar trends. These two catalysts also show similar activity for CO oxidation.

Mechanically mixed samples exhibit different selectivity patterns from the other samples (Fig. 10c). Al-3M with only 3% MnO<sub>2</sub> behaves almost like alumina. The isopropanol decomposition gives only propene and water between 250° and 400 °C. The selectivity for this reaction decreases with MnO<sub>2</sub> content but above 350 °C, the reaction goes almost completely towards propene in all the mechanically mixed samples, even those with MnO<sub>2</sub> loadings of 30%.

The selectivity towards acetone or propene measured in these steady-state experiments can be correlated with the peaks observed in the temperature-programmed desorption spectra. Both propene and acetone desorb in two peaks, one at  $\sim 100$  °C and the second between 250 - 300 °C. As the manganate loading increases, the high temperature acetone peak increases in intensity relative to the lower temperature peak. At the same time, the high temperature propene signal decreases relative to the low temperature peak. This can be correlated with an increasing selectivity towards acetone while the propene selectivity is diminished.

# Magnesia-Supported Catalysts

Magnesia, being a strong base, has a high selectivity to acetone. Hence, in the magnesia-supported samples, both the support and the overlayer are selective for acetone formation. The grafted samples show a synergistic effect, the acetone selectivity remaining high up to 500 °C. Thus, the selectivity to propene at this temperature, which is 76% over MgO and 78% over MnO<sub>2</sub>, increases to 88% in Mg-1G and 97% in Mg-5G.

As the MnO<sub>2</sub> loading increases in the impregnated samples, the isopropanol conversion approaches that of MnO<sub>2</sub>. Mg-15I and Mg-20I both show 100% acetone selectivity at low temperatures, the value decreases to  $\sim 93\%$  as the temperature is raised. Mechanically mixed samples have almost 100% selectivity towards acetone below 325 °C. Above this temperature, increasing amounts of propene are formed and the acetone selectivity falls steeply. At 450 °C, Mg-5M, Mg-10M and Mg-15M all show lower selectivity towards acetone than either magnesia or MnO<sub>2</sub>.

#### 4. Conclusion

The grafting reaction from a metal alkoxide precursor is a convenient method to synthesize overlayers of manganese with monolayer dispersion. The catalytic properties change as the support influence decreases with increasing thickness of the layer. Wet impregnation leads also to highly dispersed systems, but not to a complete coverage of the surface with the active phase. These systems have therefore a larger variation of different sites which results in a more complicated surface chemistry. Mechanical mixing follow-



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Fig. 10

Propene selectivity versus temperature for (a) grafted, (b) impregnated and (c) mechanically mixed alumina samples



ed by calcination does not yield highly dispersed manganate systems. Because of the high melting points of the manganese oxides, these species do not spread well over the surface. The differences in the overlayers formed by the three preparation methods are clearly revealed in their activity and selectivity towards CO oxidation and isopropanol decomposition respectively. The calcination temperature was found to play an important role in determining the oxidation state and the crystallinity of the overlayer.

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