Surface characterization studies of TiO₂ supported manganese oxide catalysts for low temperature SCR of NO with NH₃

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Abstract

A series of TiO₂ supported manganese oxide catalysts were prepared by wet-impregnation method for the low temperature selective catalytic reduction (SCR) of NO with ammonia as a reductant. A combination of various physico-chemical techniques such as N₂ physisorption, O₂ chemisorption, TPR, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman were used to characterize the chemical environment of these catalysts. O₂ chemisorption and XRD results suggest that Mn exist in a well-dispersed state at below 16.7 wt.% of Mn on TiO₂ anatase (Hombikat), 7.5 wt.% on TiO₂ rutile (Kemira) and P-25 (80% anatase + 20% rutile), and in microcrystalline phase above these loading levels on respective support materials. These results also reveal that Mn interacts very well with pure anatase phase compared to rutile. XPS results of Mn/TiO₂ anatase (Hombikat) catalysts illustrated the presence of MnO₂ as a major phase (peak at 642.0 eV) along with Mn₂O₃ as the minor phase at lower loadings. The presence of Mn₂O₃ disappears at higher loadings. The characterization results indicated that the manganese oxide exists as an isolated species at very low loadings, highly dispersed state probably as two dimensional monolayer species at intermediate loadings, polymeric or microcrystalline form of manganese oxide at higher (above monolayer capacity) loadings was envisaged. The catalytic performance of various amounts of Mn loaded on different TiO₂ supported catalysts for low temperature SCR reaction at catalyst bed temperature 175 °C under power plant conditions using GHSV = 50,000 h⁻¹ was studied. The catalyst with 16.7 wt.% Mn/TiO₂ anatase (Hombikat) was found to be highly active and selective catalyst for this reaction. The Raman studies acted as complimentary tool to XPS in order to characterize the manganese oxides (MnO, Mn₂O₃, Mn₃O₄, MnO₂). Raman data show that there is a strong interaction between the Mn oxides and the support, which is responsible for the impressive catalytic performance in comparison with other systems we investigated.

Keywords: TiO₂ anatase; TiO₂ rutile; MnO₂; XPS; Raman; Low temperature SCR; NO; NH₃

1. Introduction

Among the various non-catalytic and catalytic processes developed to eradicate NOₓ, the selective catalytic reduction (SCR) of NOₓ by ammonia in the presence of excess oxygen using V₂O₅/TiO₂ (anatase) with either WO₃ or MoO₃ [1–4] is by far the most important commercial process today for removing NOₓ from flue gas. This is because the catalyst has high SCR activity and is resistant to SO₂ poisoning. The predominant form of titania used is anatase. The required operating temperature for the industrial catalyst described above is typically 300–400 °C. This makes it necessary to locate the SCR unit upstream of the desulfurization and particulate control devices immediately after the steam generator in order to avoid spending money to reheat the flue gas. However, this accelerates the catalyst deactivation through exposure to high concentrations of SO₂ and small particulates. This can be avoided by locating the SCR unit at the very end of the flue gas pollution abatement units where the flue gas is relatively clean as it passes through the scrubber and the electrostatic precipitator or bag-house [5]. The advantages of tail-end configurations include catalyst exposure to a relatively clean flue gas, more space to accommodate any changes in the power cycle or fuel, a decrease in catalyst volume and hence...
cost as the result of the cleaner flue gas, and an increase in catalyst life. Some supported transition metal oxide catalysts have been investigated for the low temperature SCR reactions, which can be capable of operating in the low temperature range 80–250 °C. Amorphous chromia [6], carbon-supported vanadium [7,8], manganese [9] and copper [10,11] oxides, alumina supported manganese oxide [12], TiO\(_2\) supported chromia [13], vanadium and copper-nickel oxides supported on titania and alumina monoliths [14], show high activity for NO reduction with NH\(_3\) at low temperatures. Recently [15,16], our research group found that titania supported Mn-, Cu-, and Cr- were extremely active at 120 °C.

This paper presents a systematic study of the effects of various loadings of Mn on different phases of TiO\(_2\) supports by wet-impregnation method. In addition, these catalysts were characterized by using various physic-chemical techniques such as BET, O\(_2\) chemisorption, XRD, XPS, Raman, TPR etc., to understand the structure, oxidation/reduction properties and possible metal-support interaction of the manganese oxide species and titania support.

2. Experimental section

2.1. Catalyst preparation

TiO\(_2\) anatase (Hombikat UV 100 from Schleben) was used as support material. As determined by N\(_2\) adsorption, it had a specific surface area of 309 m\(^2\) g\(^{-1}\), a pore volume of 0.37 cm\(^3\) g\(^{-1}\), and an average pore diameter of 4.5 nm. Manganese nitrate (Mn(NO\(_3\))\(_2\)·4H\(_2\)O, 99.99%, Aldrich) was used as the source of manganese. The Mn loadings were selected from 5 to 28 wt.%. The Mn/TiO\(_2\) catalysts were prepared by a solution-impregnation method, where the required amount of manganese nitrate was added to a 100-ml beaker containing 1.0 g of support in 50-ml deionized water. The excess water was then slowly evaporated on a water bath with continuous stirring. For comparison purpose, some amount of TiO\(_2\) anatase (Hombikat) support alone was mixed in deionized water, and then water was evaporated with continuous heating and stirring. The residues, thus obtained were dried in an oven at 120 °C for 12 h, and ground to obtain homogeneous powder. Prior to the reaction studies, the powder was calcined at 250 °C for 4 h under continuous airflow (150 mL min\(^{-1}\)). Pure MnO\(_2\) and Mn\(_2\)O\(_3\) were also prepared by decomposing hydrous manganese nitrate at 420 and 680 °C, respectively. The same preparation procedure was used to prepare TiO\(_2\) rutile (Kemira, 100% rutile) and Degussa P-25 (80% anatase + 20% rutile) supported manganese oxide catalysts.

2.2. BET surface area

BET surface area of the titania and manganese loaded titania catalyst powders were measured by nitrogen adsorption at −197 °C using Micromeretics Gemini surface area apparatus. Prior to analysis, 0.05–0.1 g of catalysts was degassed at 150 °C for 2 h under helium atmosphere. The adsorption isotherms of nitrogen were collected at −197 °C using approximately six values or relative pressure ranging from 0.05 to 0.99.

2.3. X-ray diffraction (XRD)

XRD was used to identify the crystal phases of titania loaded manganese catalysts. These studies were performed on a Siemens D500 diffractometer equipped with a monochromated CuK\(_\alpha\) radiation source (wavelength 1.5406 Å). The catalysts were run 2θ ranging from 5 to 70° with step size 0.1° and time step 1.0 s to assess the crystallinity of the manganese loading. XRD phases present in the catalyst samples were identified using JCPDS powder data files.

2.4. H\(_2\) temperature program reduction (TPR)

TPR experiments were carried out on a Micromeretics Autochem I 2910. Approximately 50 mg of sample without any previous pretreatment were tested by increasing the temperature from 50 to 800 °C. The reducing gas, a mixture of 10 vol.% H\(_2\) in Ar, at a flow rate of 50 ml min\(^{-1}\), was used to reduce the catalyst with continuous temperature ramp. The temperature was then kept constant at 800 °C until the signal of hydrogen consumption returned to the initial values. The amount of H\(_2\) consumed by the catalyst sample in a given temperature range (in μmol g\(^{-1}\)) was calculated by integration of the corresponding TCD signal intensities.

2.5. Raman spectroscopy

Raman spectra of materials were taken with a Raman spectrometer (LabRam HR, Horiba Jobin Yvon Inc.) equipped with Olympus BX-41 microscope (objective \(\times 100\)) and TE-cooled CCD detector (Andor), in a backscattering configuration using He-He laser (632.8 nm excitation line) with power of 5–10 mW at a sample and spectral resolution of 0.8 cm\(^{-1}\).

2.6. X-ray photoelectron spectroscopy (XPS)

XPS was used to analyze the atomic surface concentration on each catalyst. The spectra were recorded on a Perkin-Elmer Model 5300 X-ray photoelectron spectrometer using MgK\(_\alpha\) (1253.6 eV) as a radiation source at 300 W. The spectra were recorded in the fixed analyzer transmission mode with pass energies of 89.45 and 35.75 eV for recording survey and high-resolution spectra, respectively. The powdered catalysts were mounted onto the sample holder and degassed overnight at room temperature at a pressure on the order of 10\(^{-7}\) torr. Binding energies (BE) were measured for C 1s, O 1s, Ti 2p, and Mn 2p. Recorded Auger spectra for Mn was very weak. Sample charging effects were eliminated by correcting the observed spectra with the C 1s binding energy (BE) value of 284.6 eV. An estimated error of 0.1 eV can be considered for all the measurements. The spectra were smoothed, and a nonlinear background was subtracted.
2.7. Oxygen chemisorption

The dispersion of manganese on the support surface was determined by oxygen chemisorption measurements. These measurements were performed in a pulse (Micromeretics Autochem I 2910 system) mode using He as carrier gas (30 STP cm$^3$ min$^{-1}$). Before analysis, approximately 50 mg of catalyst samples were reduced in flowing H$_2$ (50 STP cm$^3$ min$^{-1}$) at 250°C for 2 h and then flushed at the same temperature for 30 min in the He carrier flow. Then oxygen pulses (1 ml loop volume) were injected onto the carrier gas until saturation of the sample was attained. The oxygen uptake was quantified by a TCD connected to a 2910 Autochem I (Micromeretics instrument). XRD, XPS results clearly indicated that most of the manganese oxide is in MnO$_2$ phase. Based on these results, the dispersion of manganese was expressed as the atomic ratio between oxygen and manganese content equal two (O/Mn = 2).

2.8. Catalytic experiments

The SCR of NO at atmospheric pressure was carried out in a fixed bed quartz reactor (i.d. 6 mm) containing calcined catalyst (80–120 mesh). Oxygen (Wright Bros., 4.00% in He), ammonia (Matheson, 4.06% in He) and nitric oxide (Air Products, 2.0% in He) were used as received. The reaction temperature 175°C was measured by a type K thermocouple inserted directly into the catalyst bed. Experiments were performed at the GHSV 50,000 h$^{-1}$, the inlet concentrations of NO and NH$_3$ were each set at 400 ppm, and of O$_2$ remained constant (2 vol.%). The reactants and products were analyzed on-line using a Quadrupole mass spectrometer (MKS PPT-RGA), and a NO$_x$ analyzer (Eco Physics CLD 70S). The NO conversion was explained based on the difference of in-let and out-let concentration of NO divided by in-let NO concentration, whereas N$_2$ selectivity was calculated based on the concentration of N$_2$ divided by the concentration of total products in the out-let of the reaction.

$$\text{NO conversion} = 100 \times \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \quad (1)$$

$$\text{N}_2 \text{ selectivity} = 100 \times \frac{\text{N}_2}{\text{N}_2 + \text{N}_2\text{O} + \text{NO}_2} \quad (2)$$

3. Results and discussions

The BET surface area of the commercial TiO$_2$ anatase (Hombikat) sample obtained by N$_2$ physisorption at −193°C was found to be 331 m$^2$ g$^{-1}$. In order to simulate the doping process for the loading of the Mn, we exposed the titania to water followed by a calcination step at 240°C for 4 h, the surface area dropped to 239 m$^2$ g$^{-1}$. It can be explained that the crystallinity and particle size of the support material increased after calcination. The BET surface area of various amounts of Mn loaded TiO$_2$ catalysts calcined at 240°C are shown in Table 3. In the case of Mn loaded TiO$_2$ anatase (Hombikat) catalyst, a consistently decreasing trend with increasing Mn loading is noted in the series of the samples. In general the surface area of the catalyst material decreases with increasing quantity of the active component until the monolayer coverage of the impregnated component is completed [17]. However, in the case of TiO$_2$ rutile (Kemira) and TiO$_2$ (P-25) catalysts, the surface area is not changed much after calcination. The quantity of MnO$_x$ needed to cover the support surface as a monomolecular layer can be estimated from structural calculations [18]. The monolayer surface coverage is defined as the maximum amount of MnO$_x$ in contact with the oxide.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T$ (°C)</th>
<th>$T_1$</th>
<th>$T_2$</th>
<th>$T_3$</th>
<th>$T_4$</th>
<th>$T_5$</th>
<th>$T_6$</th>
<th>$T_7$</th>
<th>$T_8$</th>
<th>$T_9$</th>
<th>$T_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ anatase (Hombikat)</td>
<td>TiO$_2$ Calcined</td>
<td>405</td>
<td>591</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
<td>5% Mn/TiO$_2$</td>
<td>261</td>
<td>368</td>
<td>472</td>
<td>–</td>
<td>–</td>
<td>1279.4</td>
<td>2.81</td>
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<td>11.1% Mn/TiO$_2$</td>
<td>215</td>
<td>331</td>
<td>421</td>
<td>468</td>
<td>2148.4</td>
<td>2.36</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>16.7% Mn/TiO$_2$</td>
<td>209</td>
<td>294</td>
<td>409</td>
<td>463</td>
<td>2712.9</td>
<td>1.79</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
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<tr>
<td>20% Mn/TiO$_2$</td>
<td>207</td>
<td>308</td>
<td>409</td>
<td>459</td>
<td>3061.9</td>
<td>1.68</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>24% Mn/TiO$_2$</td>
<td>212</td>
<td>300</td>
<td>407</td>
<td>467</td>
<td>3351.0</td>
<td>1.53</td>
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<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>MnO$_2$</td>
<td>546</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
<td>–</td>
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<tr>
<td>TiO$_2$ rutile (Kemira)</td>
<td>TiO$_2$ Calcined</td>
<td>406</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>2.5% Mn/TiO$_2$</td>
<td>200</td>
<td>401</td>
<td>495</td>
<td>551</td>
<td>187.4</td>
<td>0.82</td>
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<td>5% Mn/TiO$_2$</td>
<td>236</td>
<td>272</td>
<td>414</td>
<td>480</td>
<td>535.4</td>
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<td>277</td>
<td>419</td>
<td>554</td>
<td>771.8</td>
<td>1.13</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
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<tr>
<td>10% Mn/TiO$_2$</td>
<td>277</td>
<td>287</td>
<td>412</td>
<td>554</td>
<td>1258.1</td>
<td>1.38</td>
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<td>–</td>
<td>–</td>
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<td>–</td>
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<tr>
<td>TiO$_2$ 80% anatase; 20% rutile (P-25)</td>
<td>TiO$_2$ Calcined</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
</tr>
<tr>
<td>2.5% Mn/TiO$_2$</td>
<td>195</td>
<td>274</td>
<td>386</td>
<td>462</td>
<td>468.5</td>
<td>2.06</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>5% Mn/TiO$_2$</td>
<td>194</td>
<td>286</td>
<td>404</td>
<td>459</td>
<td>803.1</td>
<td>1.76</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7.5% Mn/TiO$_2$</td>
<td>193</td>
<td>289</td>
<td>393</td>
<td>458</td>
<td>1075.2</td>
<td>1.58</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>10% Mn/TiO$_2$</td>
<td>193</td>
<td>292</td>
<td>396</td>
<td>459</td>
<td>1383.1</td>
<td>1.52</td>
<td>–</td>
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support. From the M–O bond lengths of the crystalline Mn₂O₃, monolayer surface coverage is estimated to be 0.0532 wt.% Mn per m² of the support [18]. In reality, monolayer coverage depends not only on the support surface area but also on the concentration of reactive surface hydroxyl groups apart from other preparative variables [19]. In view of these reasons, a range of Mn loadings from 5 to 24 wt.% for TiO₂ anatase (Hombikat, 239 m² g⁻¹), 2.5–10 wt.% for TiO₂ rutile (Kemira, 57 m² g⁻¹), and 2.5–10 wt.% for TiO₂ P-25 (80% anatase + 20% rutile, 58 m² g⁻¹) were selected in this investigation.

The X-ray powder diffraction patterns of Mn/TiO₂ anatase (Hombikat) catalysts of various Mn loadings calcined at 250 °C are shown in Fig. 1. Diffractograms of commercial TiO₂ anatase (Hombikat) and calcined TiO₂ alone are also included in Fig. 1. The XRD pattern of TiO₂ anatase (Hombikat) support appears to contain very sharp peaks at d = 3.54, 1.90, and 2.40 Å, which corresponds to anatase phase (JCPDS #71-1169). When the sample was calcined in air at 250 °C, its structure did not change. The Mn/TiO₂ samples with a Mn content 16.7 wt.% and above, calcined at 250 °C show X-ray reflections at d = 2.41, 1.63, and 2.11 Å (See Fig. 2) and its intensity increased gradually with the increase of the Mn loading. The appearance of XRD peaks at these d values is attributed to the formation of crystalline manganese oxide (MnO₂) phase (JCPDS # 04-0779). These results show that the XRD peaks of individual MnO₂ are absent up to 11 wt.% loading of manganese on titania anatase (Hombikat). This is a clear indication that manganese is in a highly dispersed state or the crystallites formed are less than 5 nm, and also insertion of manganese ions into the titania lattice [20] due to the presence of more surface hydroxyl groups in the titania anatase. Thus, up to 11 wt.% Mn on titania showed only the anatase phase of TiO₂. In addition, this result is in agreement with the theoretical monolayer capacity of TiO₂ support whose surface area is 237 m² g⁻¹. This is further supported from and O₂ uptake data presented in later paragraphs. As shown in Fig. 2, the XRD patterns of Mn loaded TiO₂ rutile (Kemira) clearly shows that the TiO₂ rutile peak intensity was not changed even at 10 wt.% Mn loading. This demonstrates that the manganese oxide alone possibly dispersed as in the amorphous phase. Whereas in the case of Mn/TiO₂ P-25 catalysts the XRD peak intensity decreased (Fig. 3) with increase of Mn loading, and become complete amorphous at 10 wt.% Mn on TiO₂ P-25, which is what we observed in the case of TiO₂ anatase (Hombikat) catalysts. From these results we conclude that the Mn interacts very well with TiO₂ anatase compared to rutile phase.

Temperature programmed reduction (TPR) was used in the present study to investigate the oxidation states of different loadings of manganese deposited on the TiO₂ anatase (Hombikat) support and relate these oxidation states with activity studies of the catalysts. TPR profiles of various amounts of manganese loaded titania along with bulk MnO₂ and pure support are depicted in Fig. 4. The temperature at peak maximum (T-i) and the integral H₂ consumption in the temperature range 50–800 °C is summarized in Table 1. The reduction behavior of supported manganese catalysts mainly depends upon the inherent reducibility of the pure oxide supports because the support oxide determines the reactivity of the bridging Mn–O–Support functionalities [21]. Therefore, the reduction behavior of Mn deposited on the support surface is commonly not aligned to the reduction data of the bulk MnO₂. As shown in Fig. 4, the flat TPR profile of calcined TiO₂ support indicates that this support material itself is not reducible even at high temperatures. The pure MnO₂, treated in 10% H₂-in-Ar up to 800 °C, exhibited almost a one reduction peak [22]. It should
be noted that the morphological properties of support materials (e.g., surface area, porosity), level of impurities (foreign compounds) as well as the method of preparation of MnO$_2$ may play an important role in determining the reducibility of MnO$_2$. The reduction of MnO$_2$ is influenced by the preparation procedure. In addition, the reduction temperature is also dependent on the reduction conditions, such as H$_2$ partial pressure and heating rate. It is, therefore, difficult to discuss the reduction temperature difference from the data obtained under different reduction conditions reported in the literature. The reported reduction temperatures are quite different, even for the same system in the literature. For example, Roozeboom et al. [23] have observed only a single reduction peak in their TPR of V$_2$O$_5$ studies, in contrast to the three multiple reduction peaks

![Fig. 3. XRD patterns of Mn/TiO$_2$ 80% anatase and 20% rutile (P-25) catalysts: (A) anatase phase; (R) rutile phase.](image)

![Fig. 4. TPR patterns of Mn/TiO$_2$ anatase (Hombikat) catalysts.](image)

![Fig. 5. TPR patterns of Mn/TiO$_2$ rutile (Kemira) catalysts.](image)

![Fig. 6. TPR patterns of Mn/TiO$_2$ 80% anatase and 20% rutile (P-25) catalysts.](image)
seen by Bosch et al. [24]. In accordance with this trend, the reduction of bulk MnO₂ occurred at higher temperatures than titania supported manganese due to increased diffusional limitation in bulk MnO₂ (see Fig. 4 and Table 1).

Three reduction temperature peaks were observed in the range of 200–505 °C for 5% Mn/TiO₂ catalyst, which demonstrates the manganese oxide entered into the lattice structure of titania anatase. The first peak at 261 °C was due to the reduction of Ti⁴⁺ to Ti³⁺ and Mn⁴⁺ to Mn³⁺ because of interaction with titania and manganese oxide. This suggests that the low temperature reduction peak (T-1), in the TPR profile should be assigned to the support reduction due to the interaction with manganese oxide. The other two reduction peaks of these catalysts are attributed to the reduction of Mn₂O₃ to Mn₃O₄, and Mn₃O₄ to MnO. In addition to the first three reduction peaks T-1, T-2, and T-3, a new reduction peak T-4 appeared when manganese loading was increased from 11.1 to 24 wt.% (see Table 1). However, the T-2 reduction temperature for the catalysts with 16.67 and above wt.% Mn is somewhat different than that of 11.1 and 5 wt.% Mn/TiO₂ catalysts. This is due to the fact that at lower loading manganese is incorporated into the titania lattice. The reduction peaks for catalyst 11.1 wt.% Mn/TiO₂ catalysts emerged at 215, 331, 421, and 468 °C. As explained earlier the first peak at 215 °C is due to the reduction of Ti⁴⁺ to Ti³⁺ because of its interaction with manganese oxide. In the second reduction step, MnO₂ reduces to Mn₂O₃ at 331 °C, which further reduces to Mn₃O₄ and finally reached to MnO at 421 and 468 °C, respectively. For thermodynamic reasons further reduction of MnO does not occur under the applied experimental conditions [25]. The reduction peaks for catalysts with 16.67 wt.% and higher loadings of Mn have approximately the same positions as the peaks of the 11.1% Mn/TiO₂ catalysts. All these catalysts have temperature maximum 470 °C and the signal can be attributed to Mn₃O₄, which was due to the reduction of Mn₂O₃ to MnO₄ and MnO₄ to MnO. It is expected that at a lower temperature a surface-type (probably tetrahedral) species would be reduced, whereas at a higher temperatures a more polymeric or bulk like manganese oxide would be undergoing reduction. Arena et al. [26] studied MnOₓ/TiO₂ catalyst prepared by impregnation of anatase sample with aqueous solution of KMnO₄ and calcined at 500 °C (11 wt.% Mn loading). Their TPR pattern shows main H₂ consumption at 383 °C and in high temperature region at 770 °C but without explanation about origin of such H₂ consumption. The intensity of total reduction peaks increased with the increase of manganese loading. As shown in Table 1, the total H₂ consumption decreased with increase of Mn loading, clearly indicates that the manganese oxide is dispersed well at the lower loadings. The change in average oxidation state of Mn (see Table 1), which was calculated from the total consumption hydrogen during the TPR process, continuously decreased with the increase of the manganese loading. This clearly demonstrates in Eq. (3) that the reduction process of Mn in presence of titania is assumed to take place accordingly[27]:

\[
\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}
\]

In addition to the TPR results, the X-ray diffraction data also showed the existence of MnO₂. This clearly indicates that manganese preferentially spreads on the titania anatase, up to monolayer coverage, before the formation of any bulk manganese oxide. The TPR results conclude that most of the manganese might have stabilized as Mn⁴⁺ oxidation state on the TiO₂ anatase support.

As shown in Fig. 5, the TPR reduction patterns for Mn loaded TiO₂ rutile (Kemira) displayed completely different than the TPR patterns of Mn/TiO₂ anatase (Hombikat), whereas Mn loaded on TiO₂ P-25 (80% anatase + 20% rutile) exhibited the same trend as was observed for the Mn/TiO₂ anatase (Hombikat) catalysts (Fig. 6), because of the presence of 80% anatase phase in the TiO₂ P-25 support. The TPR results indicate the interaction of MnOₓ with TiO₂ anatase phase is stronger than the rutile phase. The reduction transition appeared at different temperature, a fact that can be explained due to the presence of different titania phases. The Mn/TiO₂ Kemira

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**Fig. 7.** XPS of Mn 2p core level peak for: (A) Mn/TiO₂ anatase (Hombikat) catalysts; (B) Mn/TiO₂ rutile (Kemira) catalysts.
catalysts consumed less hydrogen up to 7.5 wt.% of Mn compared to the corresponding Mn/TiO₂ P-25 catalysts. One can see another interesting results in Table 1, the average oxidation state of Mn on TiO₂ Kemira (100% rutile) increases with increase of Mn loading, whereas it is reverse in the case of Mn on TiO₂ P-25 (80% anatase and 20% rutile), which clearly indicates that the TiO₂ anatase phase interacts strongly with Mn up to 7.5 wt.% (monolayer coverage).

TiO₂ anatase (Hombikat) supported Mn catalysts were investigated by XPS to understand the surface atomic concentration and oxidation states of Mn interacting with titania on each catalyst. Fig. 7A shows the Mn 2p photoelectron peaks of the Mn/TiO₂ anatase (Hombikat) catalysts. A significant increase in the intensity and sharpening of Mn 2p peak can be noted with increasing Mn loading. The sharpening of XPS peak intensity can be attributed to various factors including: (1) the stabilization of only one type of Mn⁴⁺ oxidation state, which strongly interacted with the support surface; and (2) more electron transfer between the active component and the support (metal-support interaction). The binding energy values of Mn 2p₃/₂ for Mn/TiO₂ anatase (Hombikat) catalysts are depicted in Table 2. In all catalysts, the binding energy of Mn 2p₂/₃ is 642 eV; it probably corresponds to MnO₂ species stabilized in all catalysts. The same phenomenon was observed in the case of Mn/TiO₂ rutile (Kemira) catalysts. Very interestingly, the intensity of the Mn 2p line significantly increased with increasing Mn loading. This increase is more prominent in the case of 10 wt.% Mn/TiO₂ rutile (Kemira), indicating that the intensity of Mn 2p photoelectron signals depends on the coverage of Mn on the TiO₂ rutile (Kemira) carrier. The stable binding energy of Mn 2p suggests that the MnO₂ species stabilized in all catalysts. The same phenomenon was observed in the case of Mn/TiO₂ anatase (Hombikat) catalysts. One can observe that the difference in binding energy between Mn 2p₂/₃ and Mn 2p₁/₂ is larger in the case of Mn loaded TiO₂ rutile (Kemira) than in the case of Mn loaded TiO₂ anatase (Hombikat). This clearly indicates that the interaction of Mn is different on different support materials, even though the oxidation state of Mn is same in both the cases.

The relative dispersion of manganese on support surface was also estimated from XPS measurement of Mn/TiO₂ anatase (Hombikat) and Mn/TiO₂ rutile (Kemira) catalysts. The surface atomic concentrations of Mn 2p, Ti 2p, and Mn/Ti ratio for both types of catalysts are shown in Fig. 8A and B. The intense signal corresponding to the Mn 2p₂/₃ level of manganese was compared with the Ti 2p₂/₃ level. The Mn 2p/Ti 2p ratio can be taken as a measure of the relative dispersion of manganese oxide on the support surface (see Fig. 8A and B). As can be noted, the surface atomic concentration of Mn increased and Ti decreased with increase of Mn loading in the case of Mn/TiO₂ anatase (Hombikat) catalysts (Fig. 8A); whereas the surface atomic concentration of both Mn and Ti increased initially for loadings up to 7.5 wt.%, and then surface atomic concentration of Mn alone decreased at 10 wt.% Mn (Fig. 8B) in the case of Mn/TiO₂ rutile (Kemira). But the increase in surface atomic concentration of Mn is more predominant compared to the Ti (Fig. 8B). In general, the surface atomic ratio of Mn/Ti is increased with the increase of Mn loading, which indicates that support surface is covered by manganese oxide (Fig. 8A and B).

The surface atomic ratio of Mn/Ti clearly explains that the Mn is intercalated in the TiO₂ anatase (Hombikat) lattice structure at lower loadings due to high surface and smaller

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Binding energy (eV)</th>
<th>Mn/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ anatase (Hombikat)</td>
<td>Ti 2p₂/₃</td>
<td>Ti 2p₁/₂</td>
</tr>
<tr>
<td>TiO₂</td>
<td>458.5</td>
<td>464.2</td>
</tr>
<tr>
<td>5% Mn/TiO₂</td>
<td>458.5</td>
<td>464.2</td>
</tr>
<tr>
<td>11.1% Mn/TiO₂</td>
<td>458.5</td>
<td>464.2</td>
</tr>
<tr>
<td>16.7% Mn/TiO₂</td>
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<td>464.2</td>
</tr>
<tr>
<td>20% Mn/TiO₂</td>
<td>458.5</td>
<td>464.2</td>
</tr>
<tr>
<td>24% Mn/TiO₂</td>
<td>458.5</td>
<td>464.2</td>
</tr>
<tr>
<td>TiO₂ rutile (Kemira)</td>
<td>TiO₂</td>
<td>458.5</td>
</tr>
<tr>
<td>2.5% Mn/TiO₂</td>
<td>458.5</td>
<td>464.2</td>
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<tr>
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<td>464.2</td>
</tr>
<tr>
<td>7.5% Mn/TiO₂</td>
<td>458.5</td>
<td>464.2</td>
</tr>
<tr>
<td>10% Mn/TiO₂</td>
<td>458.5</td>
<td>464.2</td>
</tr>
</tbody>
</table>
particle size of the support. Because of this reason, Mn is highly dispersed at a certain level called two-dimensional monolayer coverage. After reaching this level, the surface atomic ratio of Mn/Ti increased significantly on further loadings of Mn. This can be explained due to the formation of microcrystalline Mn oxide species formed on the support surface at higher loadings. XPS results clearly demonstrated that the completion of monolayer coverage takes place at approximately 16.7 and 7.5 wt.% Mn for Mn/TiO₂ anatase (Hombikat) and Mn/TiO₂ rutile (Kemira) catalysts, respectively. The results indicated that the manganese oxide exists as an isolated species at very low loadings, highly dispersed state probably as two dimensional monolayer species at intermediate loadings, polymeric or microcrystalline form of manganese oxide at higher (above monolayer capacity) loadings was envisaged. These results are in perfect agreement with XRD and TPR results that we discussed in earlier paragraphs.

Raman spectra of Mn/TiO₂ are shown in Fig. 9A–C. All Mn oxides are light sensitive [29] and we used very low laser power (5–10 mW) to avoid degradation and local heating. This point should be considered with particular attention since local heating can cause misleading shifts and broadening of the Raman modes. The peaks of Mn₂O₃ and MnO₂ located around 600–650 cm⁻¹ are overlapped with strong band of TiO₂ in this region (Fig. 9). Raman pattern of TiO₂ Hombikat support clearly showed anatase crystalline structure. The anatase
structure is tetragonal, and its conventional cell is composed by two primitive cells, each with two TiO$_2$ units and its space group is D$_{4h}^{19}$. The six modes A$_{1g}$ 519 cm$^{-1}$, 2B$_{1g}$ 399 cm$^{-1}$ and 519 cm$^{-1}$, and 3E$_g$ 144 cm$^{-1}$, 197 cm$^{-1}$, and 639 cm$^{-1}$ are Raman active. Our primary interest is the peak at 144 cm$^{-1}$ and it corresponds to E$_g$ mode of anatase. The Mn/TiO$_2$ samples show that this peak gradually decreases in intensity, becomes broader and shifts to the high frequency region with increase of Mn loading and disappeared at the concentration of Mn-oxide above 11%. The peak position and broadening compare to the larger crystalline size samples can be explained by finite size crystal using quantum confinement effect. In an ideal and infinite single crystal, only phonons near the center of the Brillouin zone contribute to the Raman spectrum because of momentum conservation between phonons and incident as well as scattered light. In addition, in fine crystals, phonons can be confined in space by crystal boundaries, and this condition produces an uncertainty in the wave vector $\Delta q = 2\pi n/L$, where $L$ is the correlation length of the phonon (or crystalline size in an ideal case), allowing phonons with $q \neq 0$ to contribute to the Raman spectrum. Unfortunately, the phonon dispersion curve of anatase has not yet been obtained experimentally or theoretically, and we cannot extend the discussion in a quantitative way at this stage. Quantum confinement effect has been recently examined by comparison size of the nanocrystals and width of the Raman band and it was shown a good correlation [30]. At low loading, Mn-oxide is form monolayer structures with Mn atoms incorporated to the crystalline lattice. It generates distortion of the crystalline lattice and, therefore, confinement effect. At concentration above 11% Mn-oxide form microcrystalline species. Because Raman cross section of Mn-oxide is relatively low, spectra becomes very weak. Raman results clearly show that formation of micro crystals on the surface occurs at 11 (and more) and 7.5 wt.% (and more) for Hombikat and Kemira, respectively. These data are in an excellent agreement with above-mentioned XRD, TPR and XPS results.

Dispersion is normally controlled by the extent of loading, nature of support and active component, and the method of preparation. To determine the dispersion of metal catalysts, the most commonly used and widely accepted method is selective chemisorption of suitable gases like hydrogen and carbon monoxide. Parekh and Weller [31,32] have devised a simple oxygen chemisorption method for determining the dispersion of equivalent molybdena area of MoO$_3$/Al$_2$O$_3$. The choice of temperature at which oxygen chemisorption could give meaningful information about the surface structure of supported metal oxide catalysts was deemed crucial. On the basis of the observation made by these researchers, it was proposed that $-196^\circ$ C (and later on $-78^\circ$ C) is the most suitable temperatures for oxygen chemisorption measurements. Subsequently, Oyama et al. [21] have proposed that if the temperature of oxygen chemisorption is around 370 $^\circ$C with a pre-reduction of the catalysts at the same temperature, results would give much more meaningful information than the results generated at $-78^\circ$ C with a pre-reduction of the sample at 500 $^\circ$C temperature. Reddy et al. [33] have also reported that the oxygen uptake measured at 370 $^\circ$C with a pre-reduction of the sample at the same temperature probably avoids bulk and over reduction of vanadium oxide and sintering of the support material. The pre-reduction temperature of catalysts was selected at 250 $^\circ$C for O$_2$ pulse chemisorption experiments in order to start with the surface reduction of support and active component. The first reason, these catalysts were calcined at low temperature, and also active for low temperature (below 200 $^\circ$C) SCR of NO reduction. Second reason, as shown in TPR patterns of all catalyst, the first reduction temperature peak appeared at below 250 $^\circ$C related to the reduction of surface interacted support and active bridge (Ti–O–Mn) component, which is very important for the activity of the catalyst. Third reason, Oyama et al. [21] have proposed that the oxygen uptake and the pre-reduction of the catalysts at the same temperature, would give much more meaningful information than the results generated by catalyst pre-reduced at different temperatures. Therefore, for our catalyst system, we have selected 250 $^\circ$C as the pre-reduction and O$_2$ pulse chemisorption temperature which gives momentous information for supported Mn based catalyst systems.

Oxygen uptake values obtained at 250 $^\circ$C on various Mn/TiO$_2$ samples are presented in Table 3. Under experimental conditions employed in this study, the pure support seems to chemisorb very small amount of oxygen. Therefore, the contribution of the pure support was subtracted from the uptake results. As seen in Table 3, the oxygen uptake value drastically increases with increasing in the manganese content up to 16.7 wt.% Mn loading and then approaches limiting value with further increase in loading. This saturation level is an indication of completion of monolayer coverage of manganese on the support surface. Whereas in the case of other two types of titanias such as TiO$_2$ rutile (Kemira) and TiO$_2$ 80% anatase, 20% rutile (P-25) supported manganese catalysts, the oxygen uptake value significantly increased up to 7.5 wt.%, then the increase in oxygen uptake value is slow at 10 wt.% Mn-loading. As we discussed in later paragraphs, the dispersion of Mn at 7.5 wt.% is higher than the 10 wt.% Mn catalysts. This clearly indicates the 7.5 wt.% of Mn is the nearest monolayer coverage on the these support materials.

The dispersion, defined as the percent of Mn-oxide units available for reduction and subsequent oxygen uptake, is estimated from the total number of Mn-oxide units present in the sample and the number of oxygen atoms chemisorbed (Table 3). The dispersion is found to increase with the increase in Mn loading up to 16.7 wt.% and started decreasing beyond this loading thus, suggesting that the Mn is dispersed as an isolated species at lower loadings, two-dimensional monolayer coverage near or just below 16.7 wt.% and dimeric or paracrystalline or microcrystalline phase at higher loadings. This is, of course, a general phenomenon with any supported metal oxide catalyst systems [33]. As shown in Table 3, the dispersion values for Mn/TiO$_2$ rutile (Kemira) and Mn/TiO$_2$ 80% anatase + 20% rutile (P-25) catalysts increased up to 7.5 wt.% and decreased at 10 wt.% Mn loading, which clearly indicates that the doping of Mn on TiO$_2$ rutile phase cannot follow a theoretical monolayer calculation rule. The results
obtained from oxygen chemisorption technique are in perfect agreement with the XRD, TPR, and XPS results described in the earlier paragraphs. As a result, valuable information like oxygen uptake and metal-dispersion and change in oxidation states of manganese can be obtained from the simple oxygen pulse chemisorption technique.

The catalytic performance of various amounts of Mn loaded on different phase of TiO$_2$ catalysts were tested for low temperature SCR at reaction temperature 175$^\circ$C. As reported in our earlier work MnO$_x$/TiO$_2$ provides respectable catalytic activity relative to the other transition metals tested at temperatures below 150$^\circ$C [15,16]. Since SCR catalysts used in power plants will typically see usage above 30,000 h/C0$_1$, all of the catalysts previously discussed were tested at 50,000 h/C0$_1$.

The NO conversion and N$_2$ selectivity results on the above mentioned catalysts were presented in Figs. 10–12. The NO and NH$_3$ conversions were zero when TiO$_2$ anatase (Hombikat) alone was used as catalysts (Fig. 10). As the manganese content increases on the support surface, the NO conversions and N$_2$ selectivity increased up to 16.67 wt.% Mn and then decreased for higher loading level. However, the NH$_3$ conversion increased with increase of Mn loading. The increasing of NH$_3$ conversion at higher loadings manganese makes the decrease in NO conversion and N$_2$ selectivity. These results clearly indicate that the conversion and N$_2$ selectivity is strongly dependent on the dispersion of manganese on the support surface. In other words, for obtaining better yields of N$_2$ a high concentration of manganese equivalent to the monolayer capacity and above on the support surface is highly essential.

As can be noted from the Fig. 10, high conversion of NO (94%) with 100% selectivity towards N$_2$ is achieved on the 16.67 wt.% Mn/TiO$_2$ Hombikat. Very interestingly, this composition is exactly corresponding to the near or just above the monolayer capacity of Mn on the TiO$_2$ anatase (Hombikat) support. As we already mentioned in the O$_2$ uptake results, the amount of manganese to achieve a monolayer coverage on a given support material can be estimated to be 0.0532 wt.% Mn per m$^2$ of the support [18]. In fact, a direct relationship was found to exist between oxygen uptakes and total conversion of NO at all Mn loadings. The catalytic performance of Mn/TiO$_2$ rutile (Kemira) showed (Fig. 11) exactly the same trend that was

![Fig. 10. Catalytic performance of Mn/TiO$_2$ anatase (Hombikat) catalysts: NH$_3$ = 400 ppm; NO = 400 ppm, O$_2$ = 2.0 vol.%; GHSV = 50,000 h$^{-1}$; catalyst wt. = 100 mg; reaction temperature = 175° C.](image-url)
observed with Mn/TiO₂ anatase (Hombikat) catalysts. However, we never observed the selectivity of N₂ to reach 100% in this case. This can be explained because the interaction of Mn with rutile phase of TiO₂ is not as good as with the anatase phase of TiO₂. As shown in Fig. 12, Mn/TiO₂ (P-25) is not as active as other two catalysts under identical operating conditions. This result is expected because the TiO₂ P-25 support material contains two types of titania phase, which cannot allow to disperse Mn properly on its surface. Even though the support material contains 80% of anatase phase, the particle size of this support is far bigger than that of TiO₂ anatase (Hombikat) support.

Additionally, industrial SCR units are exposed to significant amounts of water from combustion. As reported in the earlier work [16] Cu/TiO₂ provided high catalytic activity at 50,000 h⁻¹ and max out in activity from 200 °C. Manganese on TiO₂ was clearly most useful at temperatures below 150 °C, as its N₂ selectivity quickly declines below 95% as the temperature increases [15]. It appears that Cu/TiO₂ outperforms Mn/TiO₂ at higher space velocities when both the activity and selectivity data are considered; however, SCR units in power plants must have N₂ selectivities above 95% to avoid releasing significant amounts of N₂O into the atmosphere. Consequently, the catalytic performance of all the supported transition metal oxides tested in the presence of 11 vol.% water vapor [15]. Among all, Mn/TiO₂ provided the best overall performance when water is present. Therefore, the time-on-stream behavior of this catalyst before and after 11 vol.% water vapor was tested for 10 days (See Fig. 13). The NO conversion and N₂ selectivity of the catalyst in the absence of water decreased with time. As shown in Fig. 13, the introduction of water vapor after 24-h time-on-stream study drastically increased the selectivity of N₂ with slow decreasing of NO conversion. After certain time, the NO conversion and N₂ selectivity stabilized for throughout the time-on-stream study. This suggests that water preferentially adsorbs on the active sites responsible for the N₂O formation, and this phenomenon is beneficial for the application of Mn/TiO₂ catalysts in power plants.

4. Conclusions

Among three different types of titanias, TiO₂ anatase (Hombikat) supported 16.7 wt.% Mn catalyst is the best one for low temperature SCR of NO with NH₃. This catalyst offers 94% NO conversion, 96% NH₃ and 100% N₂ selectivity. Monolayer coverage of manganese oxide on different titania supports was determined by the most of characterization techniques such as oxygen chemisorption, XRD, XPS, Raman, and TPR. The results indicate that the completion of monolayer coverage takes place at near 16.7 wt.% Mn loading. One can conclude that results obtained from characterization techniques, the manganese oxide exists as an isolated species at very low loadings, highly dispersed state probably as two dimensional monolayer species at intermediate loadings, polymeric or microcrystalline form of manganese oxide at higher (above monolayer capacity) loadings was envisaged.
The following are the additional conclusions from this study:

1. The TiO₂ anatase appears to be a promising support material for dispersion of manganese oxide.
2. Highly dispersed Mn-oxide monolayer catalysts with Mn loadings nearly equivalent to theoretical monolayer capacity of the support material can be obtained when TiO₂ anatase is used as a support material.
3. The Mn/TiO₂ anatase catalyst is very active for low temperature SCR of NO with NH₃ in comparison to other titanias supported Mn catalysts.
4. The time of stream study of the Mn/TiO₂ anatase catalyst showed stable NO conversion and N₂ selectivity even for 10-days time-on-stream in the presence of 11 vol.% water vapor at 175 °C.

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