Catalytic pollution abatement using naturally local materials

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ABSTRACT

The catalytic conversion of the main pollutants in the exhausted gas carbon monoxide and nitric oxide to environmental friendly gas was carried out using iron and manganese ore samples. The ores have been characterized through X-ray and differential scanning calorimetry analyses. Tests for the carbon monoxide oxidation were performed in a catalytic flow system, operated under atmospheric pressure, at constant response time sixty minutes, inlet carbon monoxide 270ppm and with stepwise increase of reaction temperature from 100 to 500°C. The effect of carbon monoxide inlet concentration was also tested for higher concentrations, i.e. up to 23300ppm. Finally, to distinct the difference between the endurance ability of the most active materials, the effect of carbon monoxide inlet concentration factor, was tested. The toleration capabilities of the samples were compared at experimentally vigorous conditions; i.e. the inlet carbon monoxide concentration reached 90,000ppm. The reduction of nitric oxide (25ppm) in the presence of carbon monoxide (25ppm) and air was investigated in a catalytic flow system actuated in reaction temperature ranged from 100 to 500°C and time of stream sixty minutes. Moreover the influence of nitric oxide inlet concentration on the material activity tested. Results revealed that iron ore samples have high catalytic efficiency. In some cases, the iron ore sample, which contains relatively high iron content, is being to be more active towards both oxidation of carbon monoxide and reduction of nitric oxide.

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INTRODUCTION

Combustion of gasoline with controlled amounts of air produces carbon dioxide, water, carbon monoxide and unburned hydrocarbons. During the combustion process, high temperatures of the gasoline; results in thermal fixation of the nitrogen in the air to form nitrogen oxides.

The presence of manganese as the host cation in a catalyst of the perovskite-type was found to preferentially promote the activity of carbon monoxide-nitric oxide reaction[1].

Recently, ZrO_2-supported lanthanum, manganese oxide catalysts with varying lanthanum and manganese loading were prepared by Cimino et al.[2]. The catalytic activity was found to increase proportionally with the

lanthanium-manganese loading.

Kanji et al. investigated the reactivity and mobility of the lattice oxygen of iron oxide, in particular γ-Fe_2O_3, by ^{18}O-exchange with carbon dioxide and carbon monoxide oxidation by $^{18}O_2$[3]. The effect of the composition of mono-, bi-, and trimetallic catalysts prepared from sub-micron powders of iron-group metals on their catalytic efficiency in oxidation of carbon monoxide was investigated by Sheshko et al.[4]. Harvey et al.[5] studied the oxidation of carbon monoxide on silica-supported hematite (Fe_2O_3) by the step-response method in a tubular fixed-bed reactor, at temperatures ranging between 270 and 350ºC.

Many researches concerned with the catalytic activities of manganese catalysts focused either on the selective catalytic reduction of nitric oxide in presence of ammonia[6,7] or hydrocarbons like methane[8], propane[9], and n-octane[10].

So it is cleared that the materials whose structures contain oxide forms are most suitable ones for catalytic conversion of carbon monoxide and nitric oxide. According to that and with regard to the fact that Egypt is widely known with its riches by natural ores containing high oxides constituents (clay materials, iron ore, manganese ore, … and etc.)[11], and for succeeding in the application of the new Environmental Egyptian Legislation (codified since 1995), such study deals with the use of natural local materials for the conversion of harmful carbon monoxide and nitric oxide exhausted gases into environmental friendly gas.

EXPERIMENTAL

Two samples of iron ore from Aswan district (low and high iron contents named iron ore "a" & "b" respectively) and a sample of manganese ore from Um Bogma district were selected to carry out the catalytic conversion of carbon monoxide and nitric oxide. The ores were crushed and sieved to 10-12 meshes.

Structure and phase changes of ore sample

The ores' samples were characterized by differential scanning calorimetry (DSC) to trace the structural changes accompanying its thermal treatment. X-ray analyses were also carried out to study the crystalline structure (X-ray diffraction) and the constituents of the solid materials (X-ray fluorescence).

Catalytic reactions

The catalytic reactions of carbon monoxide, (Gas Pro. Inc., U.S.A., assay 99.98%) and nitric oxide (Gas Pro. Inc., U.S.A., assay 99.00%), were carried out in a flow type reactor operating under atmospheric pressure (Figure 1).

Operating conditions

	Oxidation reaction	Reduction reaction
Temperature (ºC):	100 - 500	
Material volume (ml):	5.0	
Inlet NO concentration (ppm):	-	25:200
Inlet CO concentration (ppm):	270:23300	25:200

1- Reactor
2- Copper heater
3- Doubly condenser
4- Receiver
5- Fe-Fe constant thermocouple
6- Temperature indicator
7- Air purification towers
8- Flowmeters
9- Gas analyzer
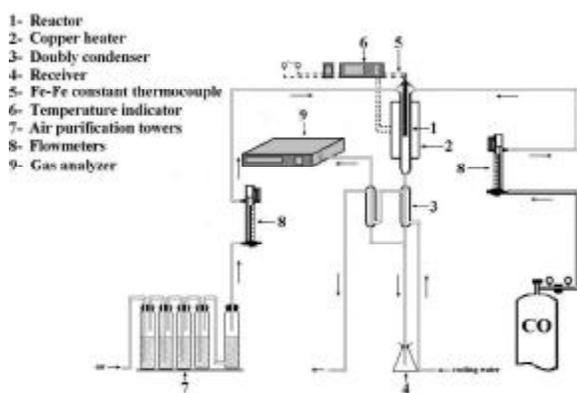
Figure 1: Catalytic flow type system

RESULTS AND DISCUSSION

1. Physical properties of the ore sample

1.2 Chemical analysis

Total silica, alumina, manganese, iron, and alkali metals contents were measured by X-ray fluorescence. The ignition loss for one gram of sample was determined at 1000ºC until constant weight was achieved.

Chemical analysis revealed that, the manganese ore sample has high iron (Fe_2O_3~51.95%) and manganese (MnO_2~28.44%) contents, low silica (SiO_2~10.10%), alumina (Al_2O_3~5.60%), calcium (CaO~0.96%) and magnesium (MgO~0.60%) contents, and the ignition loss was ~2.4%.

Chemical analysis of the iron ore (sample a) indicates that: it possesses high iron (Fe_2O_3~48%), silica (SiO_2~15.96%) and phosphorous (P_2O_5~4.59%) con-

tents, low alkali's concentration (Na_2O~0.215% and K_2O~0.086%), as well as low percentage of calcium (CaO~6.24%), magnesium (MgO~0.82%) and in addition, it contains titanium (TiO_2~0.423%). The chemical analysis of sample (b) shows that it has comparatively high iron (Fe_2O_3~63%) and manganese (MnO~3.64%) contents. Also, it possesses relatively low percentage of silica (SiO_2~10.76%), alumina (Al_2O_3~2.82%) and phosphorous (P_2O_5~0.978%) contents. The contents of other chemical constituents are approximately equal to that of sample (a).

1.2. X-ray analysis

Information concerning with the crystalline phases was obtained by comparing the characteristic spacing "d" (Å) and relative intensity "I/Io" with the data given in the ASTM cards. The X-ray diffraction patterns of the materials studied were recorded in the range 2θ = 4-90º, in a Shimadzu powder diffractometer with Cu $K_{\alpha 1}$ radiation. The instrument was operated at 40 KV and the spectra were recorded at a scanning speed of 8º/min.

The diffractogram of the manganese sample is shown in figure 2. The ore may contain the following minerals:

- **Iron oxide:** Probable amounts of goethite and hematite minerals were detected at d-distances 2.69, 2.44 and 4.21Å (goethite ASTM card No. 8-97) and 2.69, 2.51 and 1.69Å (hematite ASTM card No. 13-534) respectively. The large relative intensity I/I$_o$ of the previous diffraction apexes was consistent with the high percentage of iron minerals detected in the manganese ore by X-ray fluorescence.
- **Manganese oxide:** Our interpretation is consistent with the presence of the following manganese minerals; hausmannite (Mn_3O_4), detected at d-distances 2.69, 2.44 and 1.54Å (ASTM card No. 9-17), manganite ($MnO(OH)$) at d-distances 2.28, 2.51 and 3.40Å (ASTM card No. 8-99), pyrolusite(MnO_2) at d-distances 3.14, 1.63 & 2.44Å (ASTM card No. 12-716), and psilomelane($Mn_2O_3.nH_2O$) at d-distances 2.44, 3.40 and 1.69Å(ASTM card No.8-16).
- **Manganese silicate:** As indicated by its basic reflections at d-distances 3.14, 3.40 & 2.11Å (ASTM card no. 3-0982). The diffractograms for iron samples in figure 3 reveal the presence of different iron salts
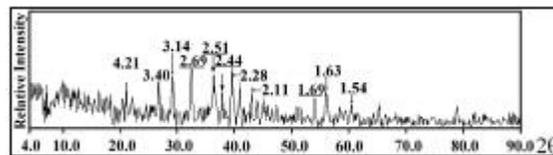
Figure 2: X-ray diffraction pattern for manganese ore sample
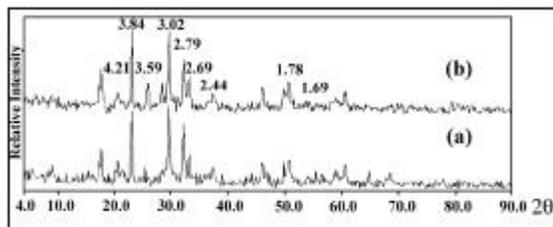
Figure 3: X-ray diffraction pattern for iron ore samples

and oxides:

- **Hematite**: Valuable amount of ferric oxide was detected at 2.69, 1.69 and 2.51Å (ASTM card no. 13-534).
- **Goethite:** As cleared by its reflections at 4.21, 2.69, and 2.44Å (ASTM card No. 8-97).
- **Siderite:** considerable amounts of Siderite were detected at 2.79, 1.69 and 3.59Å (ASTM card no. 8-133).
- **Iron silicate:** As indicated by its basic reflections at 3.02, 1.78, and 3.84Å (ASTM card no. 34-178).

On comparing between the two samples according to the different reflections and their relative intensities, it can be said that the amount of siderite and different iron oxide phases unless the ferric oxide one are more in sample (a) than that in sample (b). In other words, the hematite percentage in sample (b) is more than that in sample (a).

1.3. Differential scanning calorimetry analysis

Differential scanning calorimetry analysis is an important technique used to demonstrate the effect of heating on the performance and thermal stability of solid materials. Differential scanning calorimetry for all samples are presented graphically in figures 4 and 5 and included in TABLE 1.

Differential scanning calorimetry analysis was simultaneously recorded using a DTA-7, Perkin-Elmer apparatus. The sample was ground to 20 meshes and α-alumina was used as a reference inert material. The analysis was carried out at a heating rate of 10ºC/min in

TABLE 1: Detected endothermic peaks for iron ore samples (a) and (b) from (D.S.C.) diagram

	1st Peak	2nd Peak	3rd Peak	4th Peak
	°C(ΔH J/g)			
Sample (a)	113 (161)	294 (223)	500 (31)	661 (22)
Sample (b)	89 (84)	311 (191)	524 (12)	703 (18)
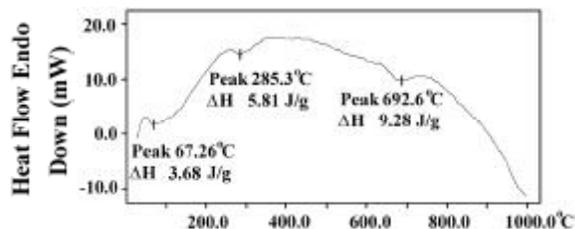
Figure 4: Differential scanning calorimetry analysis curve for manganese ore
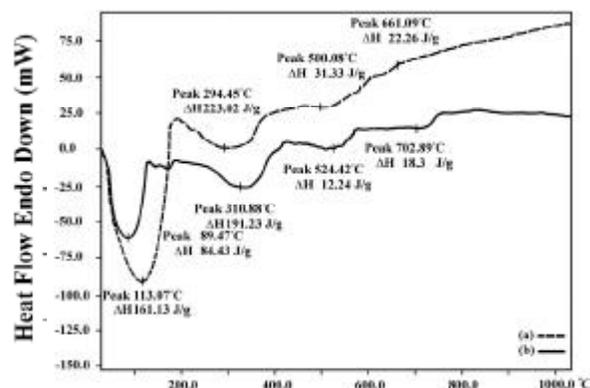
Figure 5: Differential scanning calorimetry analysis curves for iron ore samples (a) and (b)

the temperature range 25-1000ºC.

Differential scanning calorimetry for manganese ore sample (Figure 4) distinguished three endothermic valleys at ~67, ~285, and ~693ºC, the first valley occurred at ~67ºC (ΔH=3.68J/g), presents the water adsorption capacity of the ore. The second one in the range (280-339ºC) is related to the phase transformation of hydrated iron oxide, goethite, FeOOH to α-Fe_2O_3[12-14]. The third endothermic valley at ~693ºC (ΔH=9.28J/g) was related to the thermal decomposition of pyrolusite (MnO_2) into α-Mn_2O_3. The descent of the base line being at ~800ºC may be explained as the beginning of another endothermic valley resulting from the transformation of all manganese phases into hausmannite (Mn_3O_4) at high temperature, according to Earnshaw and Harrington's proposal[15].

The interpretation of the thermal analysis is consistent with the X-ray diffraction explanation.

The first endothermic peak appeared at 113 for iron ore sample (a) and at 89ºC for sample (b) represent the water adsorption capacity of the ore samples. For sample (a) the retardation of the peak and the higher heat of enthalpy (ΔH=161J/g) indicate the relative high adsorption power of this sample. The remnant three endothermic peaks are related to the phase transformation of different iron salts containing the ore. Thus, upon thermal treatment:

- The peak appeared at temperature ranged from 294 to 310ºC, related to the phase transformation of hydrated iron oxide goethite (FeOOH) to hematite (α-Fe_2O_3); and also to the decomposition of unstable $Fe(OH)_2$ to $Fe^{2+}Fe_2^{3+}O_4$ (magnetite)[12-14].

- The peak that appeared at temperature ranged from 500 to 524ºC is related to the disproportionation of meta-stable FeO to Fe_3O_4[16].

- The last peak that appeared in temperature ranged from 661 to 702ºC is related to phase transformation of siderite ($FeCO_3$) to ferric carbonate (Fe_2CO_3), which decomposed to form ferric oxide (Fe_2O_3)[17]. Also, above 600ºC iron can form interstitial compound with carbon(cementite Fe_3C)[18].

According to data in TABLE 1, the lateness of the corresponding peaks related to sample (b) is due to its higher ferric oxide content as emphasized from chemical analysis.

On the other hand, the heats of enthalpies adsorbed through the transformation of iron salts in sample (a) are higher than that occurred in sample (b), which may be due to the littleness of these salts in sample (b), as confirmed from X-ray diffraction pattern.

2. Catalytic activity

2.1. Carbon monoxide oxidation reaction

2.1.1. Effect of reaction temperature

The catalytic activity of manganese and iron ore samples towards the oxidation of carbon monoxide was carried out, at constant response time sixty minutes, inlet carbon monoxide concentration 270ppm and at stepwise increasing of reaction temperature from 100 to 500ºC. Data are graphically represented in figures 6-8.

Manganese ore sample

Data graphically represented in figure 6 cleared a moderate activity of the manganese ore at a reaction temperature 100ºC(conversion percentage ranged from ~61 to ~40% during the reaction time). Then, the activity increased about 15% at reaction temperature 200ºC.

Upon raising reaction temperature to 300ºC, the conversion increased to between ~89 and ~59%.

From figure 6 it is obvious that at reaction temperatures ranged from 100 to 300ºC, the manganese ore was very active in the first six minutes of the experiments. By comparing the activity of the material with respect to the time interval ten minutes to the end of the experiment sixty minutes, the material was steady-stable.

At 400ºC, a marked increase in the activity occurred, where the conversion reached ~96%. In addition, the same trend was observed with respect to time interval at all reaction temperatures. The manganese ore attained 100% conversion at 500ºC. The increase in catalytic conversion at the higher reaction temperature 500ºC may be due to the presence of different phases of iron and manganese oxides that act as Brönsted acid sites and consequently increase the material catalytic activity. On the other hand, the manganese ore is in the form of ferromanganese which initially contains ~28.44% MnO_2, ~51.95% Fe_2O_3, ~10% SiO_2 and ~5% Al_2O_3. On increasing the reaction temperature to 500ºC, MnO_2 decomposed to form Mn_2O_3 (as verified by X-ray diffraction), which is strong oxidizing agent. Thus, under such condition the material used is composed of Fe_2O_3 and Mn_2O_3 enclosed on the aluminosilicate structure.

Consequently, the manganese ore is rich with Brönsted acid sites and oxygen vacancies, which results from manganese and iron oxides, and as the reactant carbon monoxide is a weak Lewis base, the activity of manganese ore harmonizes its higher oxidation efficiency at the high reaction temperature 500ºC.

Iron ore sample (a)

Data in figure 7 clarified the regular increasing in the catalytic activity of iron ore sample (a) with the gradual increasing in reaction temperature from 100 to 250ºC. Whereas, the catalytic conversion was equal ~44% after the first minute of the experiment at 100ºC, then, the activity started to be in reducing manner till
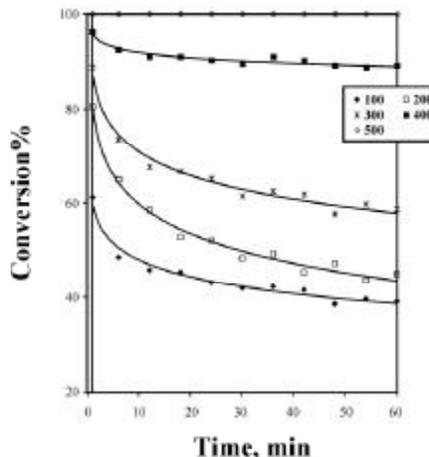
Figure 6: Effect of reaction temperature on the conversion of carbon monoxide (inlet concentration 270ppm) over manganese ore sample
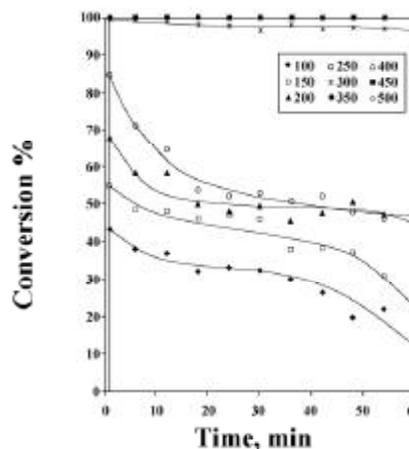
Figure 7: Effect of reaction temperature on the conversion of carbon monoxide(inlet concentration 270ppm) over iron ore sample (a)
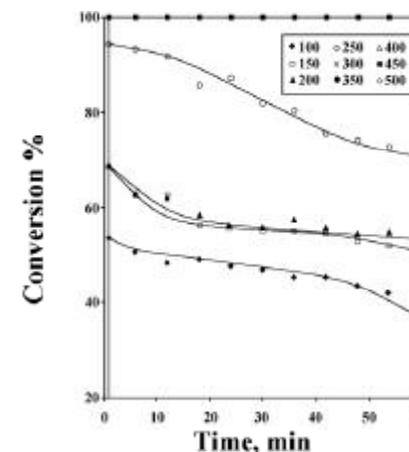
Figure 8: Effect of reaction temperature on the conversion of carbon monoxide (inlet concentration 270ppm) over iron ore sample (b)

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reached ~15% after sixty minutes. The increase in activity is sharp at reaction temperature 250ºC (i.e. increased about ~45% after sixty minutes). The increment in activity may be due to complete transformation of iron ore's constituents into the hematite one, as depicted from the thermal analysis.

The conversion values increased with the elevation of reaction temperature to the extent that it reached ~99% at 300ºC. On raising the reaction temperature to 350ºC, iron ore sample (a) achieved 100% conversion. Data in figure 7, show the relative high activity of the material in the first ten minutes of reaction temperature ranged 100-250ºC. Meanwhile, the material attained the stability stage in the last fifty minutes of each experiment, at reaction temperatures 200 and 250ºC. With continuous increase in reaction temperature to 500ºC, the material fulfilled the stability and resistance towards time influence upon the reaction activity.

As regarded to X-ray diffraction pattern and differential scanning calorimetry analysis as well as the previous results, the high activity of the ore sample may be due to the presence of different phases of iron oxides like goethite, siderite, hematite and magnetite, which acted as very strong Brönsted acid sites. Accordingly Bronsted acid sites, which are the main factor, affect the catalytic activity, increased. These results were encouraging to study the effect of reaction temperatures precisely. The iron ore sample (a) kept up its highest activity with the increase of reaction temperature to 500ºC.

Iron ore sample (b)

Figure 8 illustrated the catalytic activity of the iron ore sample (b). Data in figure revealed that at reaction temperatures 100 and 150ºC, the conversion activity of sample was higher than that of sample "a" (Figure 7) by about 10%. This may be due to the high percentage of hematite mineral in sample (b) (~64%) with respect to sample (a) (~48%), as confirmed from the ore samples' chemical analysis. This means also that the Brönsted acid sites in sample (b) increases, and consequently its catalytic activity should be more than that of sample (a).

At reaction temperature 200ºC, the carbon monoxide oxidized to the same extent on using both iron samples (Figures 7 and 8).

At reaction temperature 250ºC the activity of iron ore sample (b) increased strongly, where it ranged from ~94 to ~70% during the experimental duration time (Figure 8). According to the thermal analysis data, for sample (a), at temperature 200ºC goethite mineral started to transform into hematite one, whereas, the transformation of sample (b) goethite constituent delayed to 250ºC. This may be the reason of similarity in carbon monoxide conversion for the two samples at reaction temperature 200ºC, as well as the sharp increasing in the catalytic activity of sample (b) at temperature 250ºC.

Finally, the sample (b) accomplished 100% conversion at reaction temperature 300ºC. The complete conversion of carbon monoxide on using iron ore sample (b) attended early 50ºC than sample (a) as a result of the complete alteration of goethite mineral into hematite, in addition to the high percentage of the hematite that already exist. The material preserved its high activity with increasing of reaction temperature up to 500ºC.

From figure 8, it can be showed the stability and the resistance of iron ore sample (b) towards time influence on the reaction activity, especially at reaction temperatures ranged from 300 to 500ºC.

Effect of inlet carbon monoxide concentration

The effect of an increase in inlet carbon monoxide concentration from 270 to 23300ppm on the catalytic
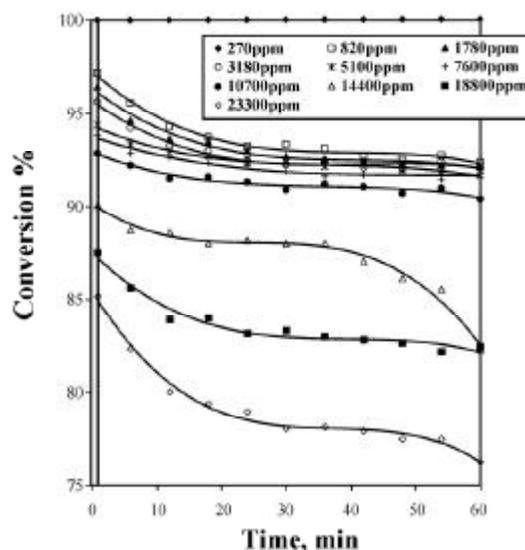
Figure 9: Carbon monoxide conversion by manganese ore sample at reaction temperature 500ºC with different carbon monoxide inlet concentrations (ppm)

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efficiency of the selected samples was determined at a reaction temperature 500ºC. Data are represented in figures 9-10.

Manganese ore sample

Figure 9 illustrates the similarity of the influence of the different inlet carbon monoxide concentrations ranging from 820 to 7600ppm. Since, the catalytic conversion of carbon monoxide decreased from ~97% to ~92% during the experimental duration time. At an inlet carbon monoxide concentration 10700ppm the conversion percentage

Whereas, iron ore sample (b) kept on complete conversion for the carbon monoxide into carbon dioxide until the inlet concentration reached 57,000ppm, after that conversion decreased with inconsiderable degree.

The resistance of iron ore samples against the higher inlet carbon monoxide concentrations may be due to the alteration of all iron phases that present in the samples into ferric oxide, upon increment in the actual reaction temperature; 500ºC to 650ºC owing to carbon monoxide-oxygen exothermic reaction.

Accordingly, iron ore sample (b) has more advantage than sample (a), at the relative high carbon monoxide concentrations, without any hesitation due to its relative high content of ferric oxide (~62wt%).

2.2 Nitric oxide reduction reaction

Nitrogen oxides emissions arise mainly from automotive sources and industrial facilities. The removal of nitrogen oxides has been at the forefront of the global environmental air pollution. Recent three-way automobile catalyst can eliminate nitrogen oxides from the exhaust of conventional gasoline engines, which operate close to stoichiometric conditions. But, one drawback of this catalyst, is that it is ineffective for nitrogen oxides removal under oxidizing conditions, which is typical of exhaust gas from lean-burn and diesel engines. Therefore, many approaches have been attempted in an effort to eliminate nitrogen oxides under oxidizing conditions by a reducing agent other than ammonia[24].

Accordingly, the reaction occurred in oxidizing environment, i.e. in the presence of purified air (21vol.% oxygen), this vigorous environment is similar to or may be more difficult than that present in the outlet of car engine.
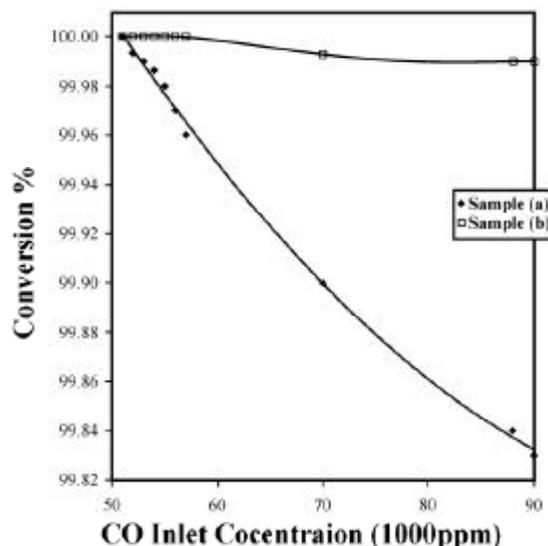
Figure 10: Comparison between iron ore samples for the carbon monoxide conversion at reaction temperature 500ºC with different carbon monoxide inlet concentrations at interval time one minute
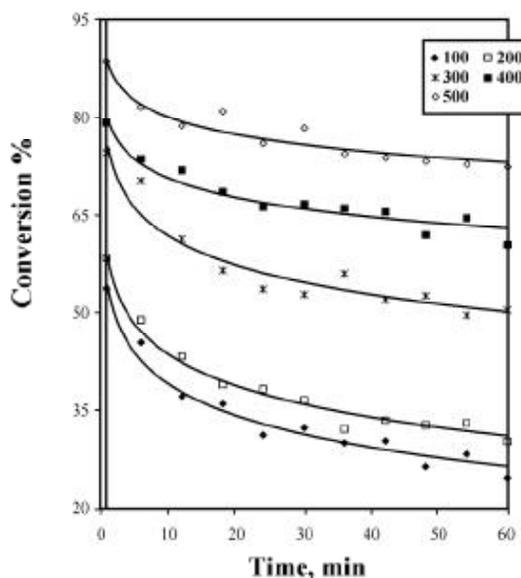
Figure 11: Effect of reaction temperature on the conversion of nitric oxide (inlet concentration 25ppm) over manganese ore sample

Effect of reaction temperature

The catalytic activity of ores' samples towards the reduction of nitric oxide in the presence of carbon monoxide and air stream was studied at reaction temperatures 100, 200, 300, 400 and 500ºC. The influence of each temperature was tested for sixty minutes in the presence of 25ppm nitric oxide as well as 25ppm carbon monoxide gas. Data are illustrated graphically in

figures (11-13).

Manganese ore sample

Figure 11 clarified the moderate activity of the material at reaction temperatures 100 and 200ºC, where the catalytic reduction decreased gradually from ~55 to ~25% and from ~60 to ~35% respectively, during the reaction duration time. This moderate catalytic activity may be related to the presence of psilomelane mineral ($Mn_2O_3.nH_2O$) in the ore, which challenge the catalytic reduction of the nitric oxide[25]. Decreased slightly, where it ranged from ~93% to ~90%. After that, a remarkable diminution in manganese ore efficiency was observed at the high carbon monoxide concentration 14400ppm.

With gradual increase in the inlet carbon monoxide concentration to 18800ppm then to 23300ppm, the material kept on loss its efficiency. On the other hand, the effect of the response time on the catalytic conversion was enlarged, where the conversion of 18800ppm decreased for about ~4% (i.e. from ~87% to ~83%) whereas, it decreased ~9% (i.e. from ~85% to ~76%) for inlet carbon monoxide concentration 23300ppm.

Iron ore samples

The experimental data clarified the high efficiency of both iron ore samples (a and b), in such a manner that the materials maintained the complete catalytic conversion of carbon monoxide into carbon dioxide in spite of the increasing in inlet carbon monoxide concentration.

On the other hand, the materials kept its ability for the complete conversion; i.e. 100% catalytic oxidation, during the experimental duration time (the sixty minutes), even at the higher inlet carbon monoxide concentration 23300ppm.

From results it obvious that all ores' samples have strong positive effectiveness towards the catalytic oxidation of the carbon monoxide gas into carbon dioxide one. The activity of these materials may be explained according to the following suggested mechanism:

$$: CO_{(gas)} \rightarrow CO^+_{(ads.)} + e^-$$

$$\frac{1}{2}O_{2(gas)} + e^- \rightarrow O^-_{(ads.)}$$

$$2\ O^-_{(ads.)} + CO_{(ads.)} \rightarrow CO^{-2}_{3(ads.)}$$

$$CO^{-2}_{3(ads.)} + CO_{(ads.)} \rightarrow 2CO_{2(gas)}$$
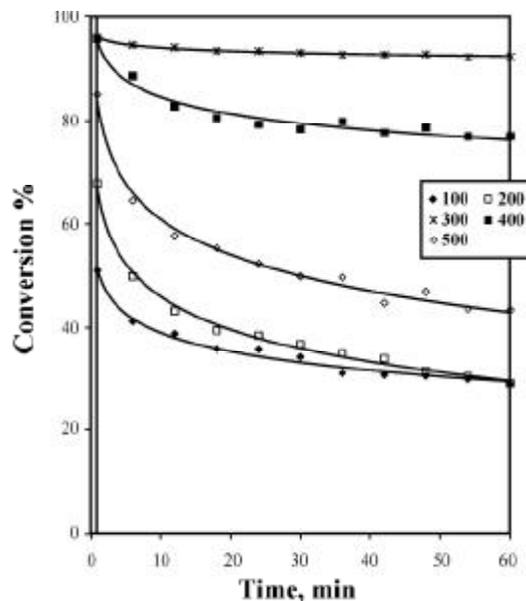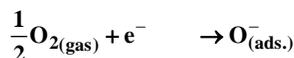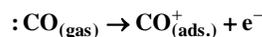
Figure 12: Effect of reaction temperature on the conversion of nitric oxide (inlet concentration 25ppm) over iron ore sample (a)
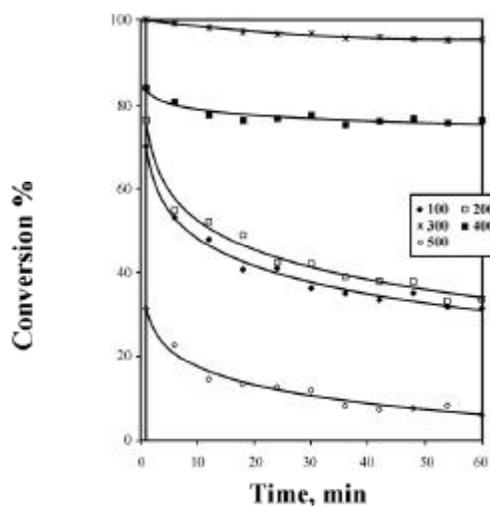
Figure 13: Effect of reaction temperature on the conversion of nitric oxide (inlet concentration 25ppm) over iron ore sample (b)

- Carbon monoxide is a weak Lewis base bears a lone pair of electrons on its carbon atom. It acts as a donor towards transition metal (as iron and/or manganese).

- The mechanism of the reaction is performed through the chemisorption of carbon monoxide on the transition metal constituting the ores (iron an/or manganese), via the lone pair of electrons of carbon monoxide molecule; high electron density can thus be de-

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localized into the transition metals[12].

- The reaction is carried out through the formation of CO_3^{-2}, carbonate intermediate, which also chemisorbed on the active sites (i.e. transition metals)[19-21].

- During the reaction, an intermediate compound is formed, that compound is CO_3^{-2}. This compound is stable at low reaction temperature as well as in the presence of carbon monoxide and oxygen compounds. While at reaction temperature 350ºC, CO_3^{-2} is easily break down[22].

- Catalytic oxidation of carbon monoxide into carbon dioxide is a reversible reaction at the relative low reaction temperatures[14].

$$2CO \rightleftharpoons C + CO_2$$

However it is obvious that both iron ore samples have strong effectiveness towards the catalytic oxidation of the carbon monoxide into carbon dioxide.

The higher activity of iron ore may be related to:

- The presence of different iron oxide phases like Fe_2O_3, FeOOH and Fe_3O_4, which contain Fe^{+3} cations (Brönsted acid), increases its affinity to react with a weak Lewis base. Carbon monoxide is a weak Lewis base and acts as a donor towards transition metal, the vacant orbitals accept electron density from fill metal orbitals to form a type of π bonding that supplements the σ bonding arising from lone pair donation, high electron density on metal atom can thus be delocalized into the transition metal.

- Most of iron salts are oxidized to α-Fe_2O_3 (in which, oxygen ions are hexagonal close packed and the Fe^{+3} ions are present in octahedral holes) and Fe_3O_4. The activity of Fe_3O_4 is related to the transfer of electrons between Fe^{+2} ions occupying the octahedral holes and Fe^{+3} ions in the tetrahedral holes in the crystal lattice of Fe_3O_4[23].

- The attachment of Fe^{+2} and Fe^{+3} ions with strong electron attracting group like O⁻, increases the electron deficiency of iron cations Brönsted acid sites increase as well as the their affinity for carbon monoxide catalytic oxidation.

- The mutual transfer of electrons between Fe^{+2} and Fe^{+3} ions increases the catalytic activity of Fe_3O_4 as well as the ore activity.

So, for the previous reason, both samples were subjected to carry out the catalytic oxidation of high inlet carbon monoxide concentrations at reaction temperature 500ºC.

Each experiment continued just for one minute, due to the extreme heat emitted from the reaction, which occurred as a result of the exothermic nature of the carbon monoxide-oxygen oxidation reaction. This heat elevates the reactor temperature from 500ºC to be measured at 650ºC. This relative high reaction temperature is suitable enough to convert most of the different iron phases (exist in the ore) into ferric oxide as clarified from differential scanning calorimetry data (Figure 5 and TABLE 1).

Data in figure 10 clarified the slight decreasing in the catalytic efficiency of iron ore sample (a) with the continuous increase in the inlet carbon monoxide concentrations from 51,000 to 90,000ppm, i.e., the conversion became 99.83% for 90,000ppm.

The rule of psilomelane mineral can be explained according to Harvey et al.[26] that, the catalytic reduction of nitric oxide by carbon monoxide depends on the rule of surface oxygen vacancies, as well as the high oxygen lability detected on Mn_2O_3 surface according to Tatsuji and Albert's suggestion[25].

Upon increasing the reaction temperature to 300ºC, the catalytic activity increased sharply, whereas the reduction varied from ~75 to ~57%. Continuous increment in the catalytic activity of the material was occurred on raising the reaction temperature to 400ºC, the conversion reached ~64% at the end of the experiment duration time. The maximum activity of manganese ore was extended at reaction temperature 500ºC, where the catalytic reduction of the nitric oxide gas became ~75% after sixty minutes.

According to Harvey et al.[26] and in agreement with the detected mineralogical structure of the manganese ore as confirmed by X-ray diffraction and differential scanning calorimetry analyses (Figures 2 and 4), it can be said that the gradual increasing in the catalytic activity of the manganese ore with the continuous increase in the reaction temperature may be related to the thermal decomposition of MnO_2 (Pyrolusite) into α-Mn_2O_3, and also the formation of magnetite (Fe_3O_4) during the thermal decomposition of goethite (FeOOH) and the unstable $Fe(OH)_2$.

Iron ore sample (a)

Iron ore sample (a) achieved moderate catalytic activity at low reaction temperature 100ºC, where the catalytic reduction decreased gradually from ~51 to ~30%, during the reaction duration time (Figure 12).

By raising the reaction temperature to 200ºC, the ability of iron ore material for catalytic reduction increased slightly whereas the conversion ranged from ~68 to ~30%.

The material reached its maximum catalytic activity at reaction temperature 300ºC, where the nitric oxide was reduced by ~96% after the first minute of the reaction. At the same time, iron ore showed its highest resistance against the influence of reaction time on the catalytic activity where the reduction percentage decreased by ~4% at the end of the reaction, i.e. after one hour.

On further increase in the reaction temperature to 400 then to 500ºC, the catalytic activity of iron ore material starts to decrease and the conversion of nitric oxide reached ~84 and ~48% respectively after the duration time. The decrease in the catalytic reduction may be related to the point that the magnetite mineral is re-oxidized to form hematite (Fe_2O_3), which is less active for the reduction of nitric oxide, in the presence of the reductant carbon monoxide. The role of carbon monoxide is to reduce the catalyst in order to maintain a sufficient concentration of surface oxygen vacancies for nitric oxide reduction.

Iron ore sample (b)

Data in figure (13) represented similar moderate catalytic activities on using iron ore sample (b) at reaction temperatures 100 and 200ºC, where the catalytic reduction of nitric oxide decreased gradually from ~70 to ~38% and from ~76 to ~40% respectively, during the reaction duration time.

By raising the reaction temperature to 300ºC the ability of the material attained its maximum value for the catalytic reduction of nitric oxide, whereas the conversion ranged from 100 to ~96%, during the reaction duration time.

The catalytic activity decreased gradually at reaction temperature 400ºC (it reached ~80% after sixty minutes). Sharp decrement occurred in the catalytic conversion at reaction temperature 500ºC, where the reduction value of nitric oxide ranged from ~31 to ~8% during the reaction duration time (Figure 13). The decrease in the activity may be due to the re-oxidation of magnetite to form hematite as discussed before.

The catalytic activity of iron ore sample (b) towards the reduction of nitric oxide, at the reaction temperatures 400 and 500ºC, was relatively less than that on using sample (a).

On the other hand, this is related to the fact that iron ore sample (b) contains more percentage of hematite minerals (according to chemical analysis), in addition, to that formed upon the re-oxidation of magnetite at such reaction temperatures (400 and 500ºC) as verified by X-ray diffraction and differential calorimetry analyses.

Effect of inlet nitric oxide concentration

The influence of reactants concentration on the catalytic activity of different ores' samples for catalytic reduction of nitric oxide was evaluated, at the optimum reaction temperature for each sample, with inlet concentrations of nitric oxide 25, 50, 100 and 200ppm. The catalytic activity of each material was tested for sixty minutes. Data are illustrated graphically in figures (14 -15).

Manganese ore sample
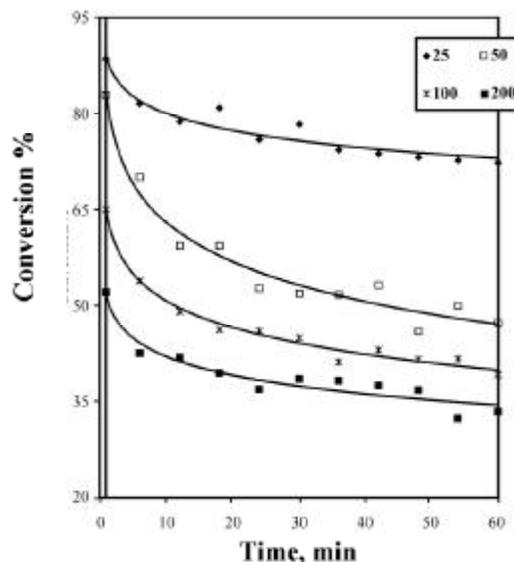
Figure 14: Nitric oxide conversion by manganese ore sample at reaction temperature 500ºC with different nitric oxide inlet concentrations (ppm)

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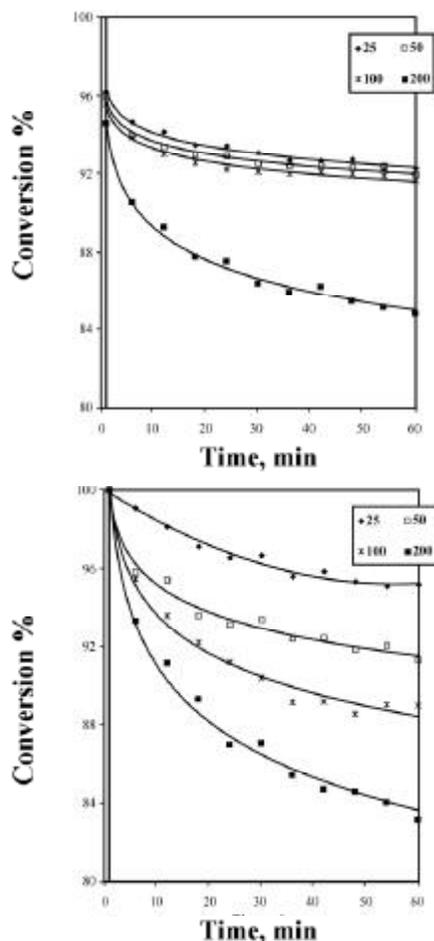
Figure 15: Nitric oxide conversion by iron ore samples (a) and (b) at reaction temperature 500ºC with different nitric oxide inlet concentrations (ppm)

Figure 14 clarified that the manganese ore, at the optimum reaction temperature 500ºC, have moderate catalytic activity at inlet nitric oxide concentration 50ppm, since the conversion percentages reached ~50 after sixty minutes of the reactions. With the continuous increase in the inlet concentration of nitric oxide to 100 and then to 200ppm, the catalytic activity of the material decreased gradually, whereas the conversion reached ~34% at the end of the reaction, i.e. 200ppm.

Iron ore samples

Figure 15 represented the slight relative superiority of iron ore sample (b) with respect to sample (a) through the different inlet concentrations of nitric oxide at reaction temperature 300ºC, especially in case of 200ppm, where the conversion percentage varied from ~100 to ~83% while in case of sample (a) it varied from ~96 to

~86%.

The high activity of the local iron ore material is related to the fact that, the iron species exposed to the surface are in different crystalline forms "orthorhombic, octahedral, …etc." (as confirmed by X-ray diffraction patterns), i.e. formation of surface active spinal, which is responsible for the high activity.

Carbon dioxide and nitrogen, all go through a maximum at the beginning of the reaction duration time indicating that the initiated state of material has a higher activity as compared to the steady state.

CONCLUSION

From results it can be concluded that:
- Iron ore samples have high catalytic efficiency.
- The iron ore sample, which contains relatively high iron content, is being to be more active towards both oxidation of carbon monoxide and reduction of nitric oxide.

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