

Effect of Redox Nature of Impregnated Ferrite Catalysts on Their Carbon Monoxide Oxidation Activity.

TD Radhakrishnan Nair^{a*}, and CU Aniz ^{a,b}

^aSchool of Chemical Sciences, Kannur University-670 327, Kerala, India.

^bR & D Division, Sud – Chemie India Pvt Ltd., Binanipuram-683 502, Kerala, India.

Research Article

Received: 19/09/2013

Revised: 27/09/2013

Accepted: 30/09/2013

*For Correspondence

School of Chemical sciences,
Payyanur Campus, Kannur
University, Edat.P.O, Kannur-
670327, Kerala, India.
Telephone: +91 497 2806402
Fax: +91 497 6802402

Keywords: Ferros spinels,
Palladium impregnation, Redox
nature, CO oxidation activity

ABSTRACT

Ferrite catalysts of Nickel, Cobalt and Copper were prepared by co-precipitation hydrothermal route and were impregnated with Palladium, Cerium and Lanthanum as promoters. These were characterized and found to be thermally stable. Both the ferrites and the impregnated samples were tested for carbon monoxide oxidation activities and the results correlated with the reducibility of the catalysts using temperature programmed reduction (TPR) studies. The reduction step of hematite phase of ferrites to magnetite was found shifted to lower temperature region and the catalytic activity was found to be enhanced upon Pd impregnation. The reason for the improved catalytic activity is explained on the basis of preferential adsorption, the strong synergic effects between the different metal components and the relative changes in the redox nature of the catalysts.

INTRODUCTION

The ever growing demand for catalyst materials with desired properties in the field of environmental purification continues to prompt researchers globally for developing newer and newer materials. This is particularly necessary in the case of catalysts for use in automobile exhaust pollution control systems to protect the precious atmosphere. The significant aspect is that when a petrol engine starts from cold state, the exhaust manifold including the catalytic converter will be cold and hence the catalyzed reactions in the exhaust chamber are kinetically limited during 'cold start'. Hence the harmful pollutants like carbon monoxide, due to its incomplete combustion, get released through the exhaust into the atmospheres before the catalyst system could reach the light off point where the oxidative conversion exceeds 50 percent.

Noble metal catalysts like platinum, palladium, rhodium, gold etc supported on ceria or alumina with good dispersions are currently being used as emission control three way catalysts. Even though a properly synthesized noble metal catalyst can give full CO conversion even at ambient reaction temperature ^[1, 2], they are expensive and susceptible to sintering. Here lies the importance of developing and testing the cheaper and efficient materials ^[3]. The use of the ferrite spinels assume significant in such a context ^[4,5,6].

The oxidative capacity of some base metal oxides were reported earlier and their activity has been found enhanced by the addition of promoters like Palladium by impregnation ^[7, 8]. Catalyst compositions with noble metal and base metal oxides, like Pd-(Cr, Cu)/(Ce, Zr)O_x/Al₂O₃, Pt-(MnO_x, CoO_x)/SiO₂, Co-(Pt, Pd, Rh)/Ce-Al-O(Al₂O₃), Pd-(Fe, Mn,Co, Ni,Cu)-O_x/NaZSM-5 and Pd/(Mn₂O₃ + SnO₂) systems for oxidation applications are thus getting attention these days ^[9,10,11,12,13,14]. A series of catalyst preparations can be seen by impregnation with Cobalt and Lanthanum on to monolith catalysts to improve the redox properties as an attempt in this direction ^[15].

Catalyzed oxidation of CO is being extensively studied as an environment 'greening' process. The Mars van Krevelen mechanism explains the redox pathway where the lattice oxygen of the catalyst is consumed during the oxidation of CO. The change in the redox properties of the metal oxides when new elements are incorporated to them are discussed in literature [16]. Examples like Ni incorporation on to Cu/Zn/Al catalyst and Cu addition to CeO₂ systems are studied to show their effect on redox properties as well as the catalytic reaction rates [17, 18]. The effect of Palladium loading on the redox properties and the catalytic activities of various ternary compositions of copper, chromium and aluminum are also studied recently [19].

The present work is an attempt for improving the performance of the ferrite spinel catalysts for carbon monoxide oxidation by incorporating metals like palladium, to modify the redox properties of ferros spinels in a beneficial way.

EXPERIMENTAL

Preparation of catalyst samples

Pure ferrite catalysts of Ni, Co and Cu are prepared via co-precipitation method using Ferric chloride, Nickel acetate, Cobalt acetate and Copper acetate as respective metal precursors and NaOH as the precipitating alkali. Calculated amount of NaOH is taken as the base stock and the aqueous solutions of metal precursors at the above mole ratios are added from overhead slowly with thorough mixing. Co-precipitation was done at room temperature at pH 11.5. After the precipitation, the slurry was kept for 10 minutes at autogenous temperature of 40°C, the temperature was then raised to 90°C and kept for 40 minutes with a temperature control of +/- 5°; always maintaining the slurry concentration with hot de-ionized water. The slurry was filtered and warm water washes were given to remove chloride and other impurities. Samples were dried at 100°C for 4 hrs and used for powder X-ray diffraction (PXRD) studies to check the formation of spinel phase. A portion of each sample was calcined at 300°C for 4 hrs and sieved (75 µm). These powders were made into pellets by applying mild compaction and further granulated to ~1mm diameter to use in catalytic performance evaluations.

Incorporation of promoters onto the catalyst samples

A portion of the simple ferrites dried at 100°C were used for the impregnation studies. Nitrate salts of Palladium, Cerium and Lanthanum were dissolved separately in calculated quantity of de-ionized water to get clear solutions. Incipient impregnation method was applied to incorporate the promoter metals on the oxide samples as discussed elsewhere [20]. The targeted concentration of the promoters was 0.3% w/w. Samples were then calcined at 300°C for 6 hrs to complete the calcination process to confirm the removal of nitrates.

Characterization of samples

The prepared samples were characterized by PXRD, N₂ adsorption, Temperature programmed desorption using Ammonia (NH₃-TPD), Atomic Absorption Spectroscopy (AAS), Thermogravimetry (TG/DTA), TPR, Scanning Electron microscope (SEM) etc. TPD and TPR studies were done using *Pulse Chemisorb 2705*, Micromeritics. For NH₃-TPD, 5 % NH₃ in helium gas (Bheruka gases) was used as the adsorbate, where as for TPR, 10% H₂ in nitrogen gas (Bheruka gases) was used as the reactive gas mixture. Temperature of the samples was raised to 800°C at a rate of 10°C/min, monitoring the sample outlet at calibrated thermal conductivity detector (TCD). Nitrogen adsorption-desorption measurements were done on a volumetric Micromeritics *Tristar* apparatus at liquid N₂ temperature, 77.3K and BET/BJH methods were used for the calculation of surface area and pore volume respectively. In addition to the gas purification stations for all the input gases, a cold trap was connected during TPR run to remove the moisture formed during the reaction.

Granules of ~1mm diameter were used for the CO oxidation test to avoid pressure build up with powder samples, maintaining the space velocity of ~30000. Calibrated gas mixture of 1%CO and 6%O₂ in balance N₂ gas (Bheruka gases) was used as the inlet feed. Both inlet and outlet gases were analyzed using gas chromatograph (GC) equipped with flame ionization detector (FID) and methenator. The experimental methods and characterization details are described earlier [21]. For all the dynamic experiments, the sample mass, rate of gas flow, reactive gas composition etc were optimized to agree with the standard criteria to avoid mass transfer limitations and hydrogen thin situations [22, 23]. The samples were tested for the CO oxidation under similar conditions of experimental set up and sample preparation explained above.

RESULTS AND DISCUSSION

Elemental compositions of the samples were in agreement with the targeted figures showing the absence of leaching of metallic ions during the preparation and washing stages. The formation of the spinel phase is confirmed by the X-ray diffraction experiments. The typical peak value corresponding to $2\theta = 35.5$ represents the characteristic 311 plane for spinels. The XRD patterns are quite similar for the pure and mixture samples and this trend is expected due to the similarities among the +2 valence state of metal ions present in the mixed samples [21]. TG patterns of the ferrites showed good thermal stability of the samples even above 700°C during air oxidation. The low temperature weight losses up to 300°C are related to free moisture as well as bound water of crystallization. The BET surface areas of all the samples are given in Table-I. The surface area of CoFe_2O_4 is $138\text{m}^2/\text{g}$ and that of CuFe_2O_4 is $116\text{m}^2/\text{g}$. These samples have higher surface area values if we compare with similar samples prepared through nitrate route [21], matching to the relatively higher pore volume and lower APD values. The average particle size from SEM is $5\ \mu\text{m}$ for the NiFe_2O_4 , CoFe_2O_4 and CuFe_2O_4 ; their porous and aggregate nature is clear from the SEM images given in Figure-1.

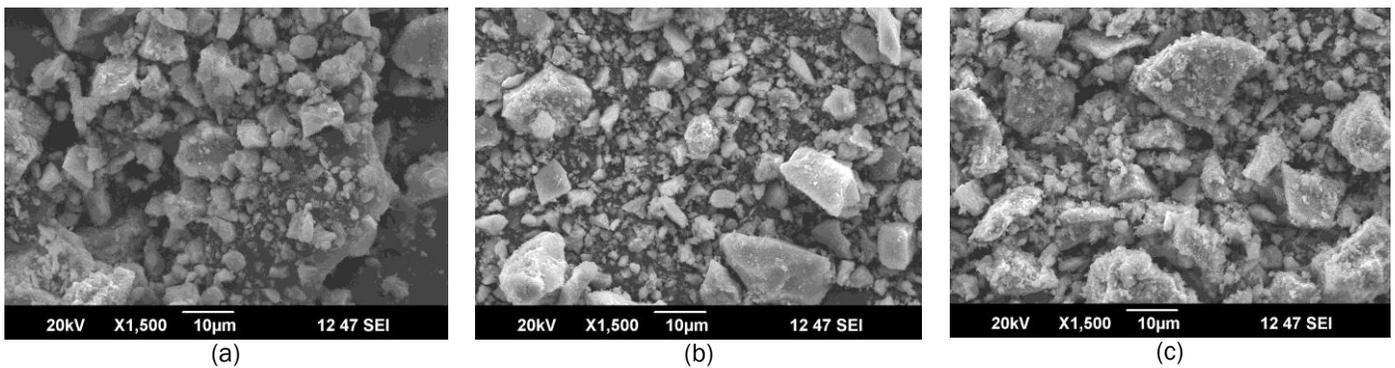


Figure 1: SEM images of pure (a) NiFe_2O_4 (b) CoFe_2O_4 and (c) CuFe_2O_4 ferrite samples calcined at 300°C

Average pore diameter values obtained from the BJH N_2 adsorption experiments are plotted in Figure-2. All the samples have pores in the meso-porous range, with well-defined step and Type IV hysteresis loop due to capillary condensation, originate from the secondary inter particle voids between their aggregates. These observations are in line with the observations from the SEM analysis. The IR spectra showed two absorption bands at 500 and 700 cm^{-1} each arising from inter atomic vibrations which are the characteristics of spinel ferrites.

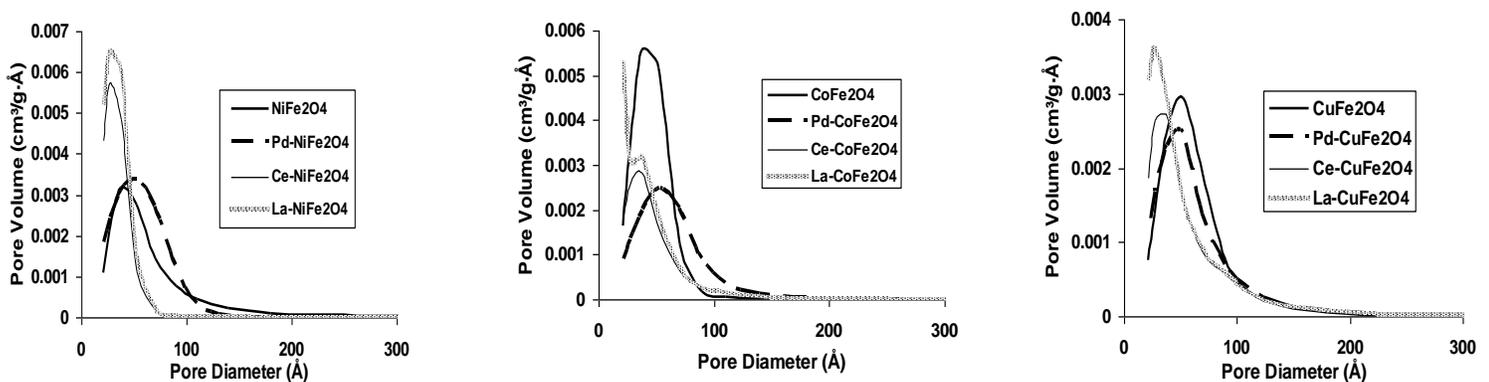


Figure 2: Average Pore diameter distribution of pure and Pd/Ce/La doped NiFe_2O_4 , CoFe_2O_4 and CuFe_2O_4 calcined at 300°C

AAS analysis to estimate the impregnated trace metals showed matching results to the expected composition of 0.3% w/w within $\pm 3\%$ variation, confirmed the proper incorporation of promoters into the samples. All the samples gave similar patterns in thermogravimetric experiments and showed that the promoters do not alter the catalyst pore structure significantly during calcination due to heat changes. However, the presence of the different metal ions on the surface of the spinel samples affect surface area, porosity etc. The BET surface areas of the samples showed variations after impregnation and calcination at 300°C (Table-I). Surface area of the Pd impregnated samples got reduced and the Ce impregnated samples did not exhibit any change. The La impregnated samples showed increase of surface area. The mean pore diameter of the samples also shifted slightly towards micro pore size in this case as shown in Figure-2.

Table I: Physico-Chemical properties of Pure NiFe₂O₄ (a) CoFe₂O₄ (b) CuFe₂O₄ (c) and their Pd/Ce/La doped samples.

(a)

Sample Name	NiFe ₂ O ₄	0.3Pd NiFe ₂ O ₄	0.3Ce NiFe ₂ O ₄	0.3La NiFe ₂ O ₄
BET SA, m ² /g	132	134	141	231
Langmuir SA, m ² /g	249	258	310	368
t-plot Ext SA, m ² /g	141	174	224	278
PV BJH, ml/g	0.189	0.225	0.169	0.201
APD BJH, A ^o	50	48	31	32

(b)

Sample Name	CoFe ₂ O ₄	0.3Pd CoFe ₂ O ₄	0.3Ce CoFe ₂ O ₄	0.3La CoFe ₂ O ₄
BET SA, m ² /g	138	114	110	189
Langmuir SA, m ² /g	353	181	174	223
t-plot Ext SA, m ² /g	207	117	130	157
PV BJH, ml/g	0.231	0.167	0.124	0.146
APD BJH, A ^o	42	53	42	38

(c)

Sample Name	CuFe ₂ O ₄	0.3Pd CuFe ₂ O ₄	0.3Ce CuFe ₂ O ₄	0.3La CuFe ₂ O ₄
BET SA, m ² /g	116	118	117	161
Langmuir SA, m ² /g	212	187	187	257
t-plot Ext SA, m ² /g	220	124	140	182
PV BJH, ml/g	0.17	0.168	0.151	0.174
APD BJH, A ^o	51	52	45	41

The TPR studies of the pure ferrite samples calcined at 300°C were done and the results are given in Figure-3(a), Figure-3(b) and Figure-3(c); the profiles of pure ferrites are shown magnified for easy read-out. The respective reduction peaks of metal ions present and their peak positions are well matching with the earlier data [21, 24]. It is interesting that all the three simple ferrite samples got exactly similar TPR pattern in comparison with those prepared through nitrate routes. The low temperature peak profile in each sample not only represents the reduction of divalent metal ions but also includes the initial reduction stages of Iron oxides [25, 26].

Carbon monoxide oxidation profiles of the samples are given in Figure-4(a), Figure-4(b) and Figure-4(c). CuFe₂O₄ showed the maximum CO conversion activity at low temperatures compared to CoFe₂O₄ and NiFe₂O₄. The performance of the samples follow same trends of conversion compared to similar samples prepared via nitrate route and it validate the influence of the inherent activities by the divalent ion in the octahedral positions. However, the former possess relatively lower conversion values only, might be due to retention of small amounts of chloride ions on the surface of the catalyst samples even after thorough washing. The presence of relatively bigger chloride ions on the catalyst surface might deter the adsorption of CO molecules for oxidation. This is in line with the operation of the Mars van Krevelen mechanism probable for the CO oxidation on spinels [16].

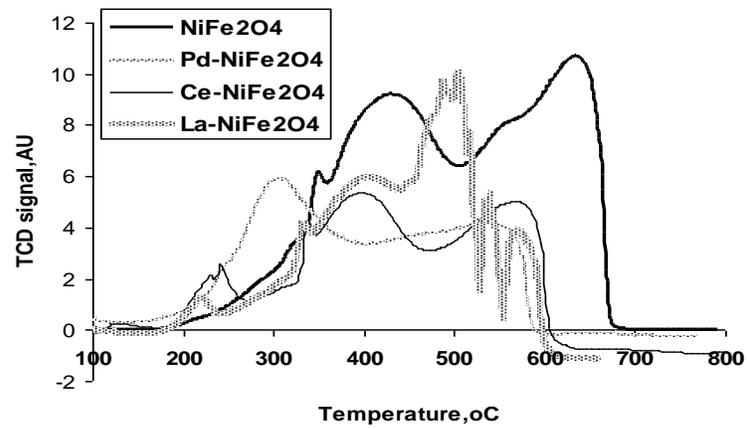


Figure 3(a): TPR profiles of pure and Pd/Ce/La doped NiFe₂O₄ calcined at 300°C

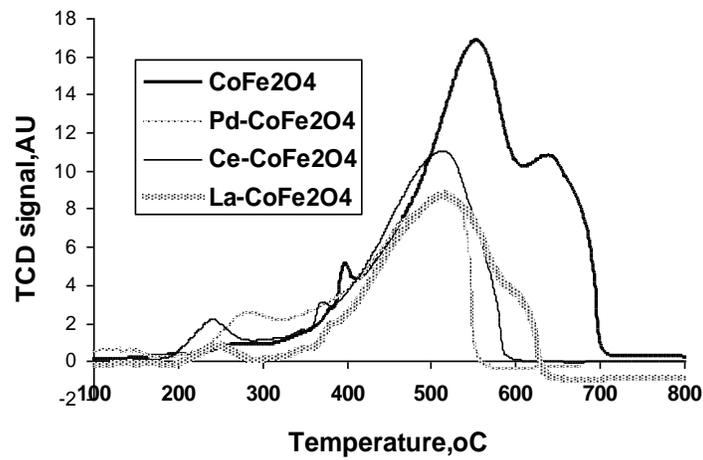


Figure 3(b): TPR profiles of pure and Pd/Ce/La doped CoFe₂O₄ calcined at 300°C

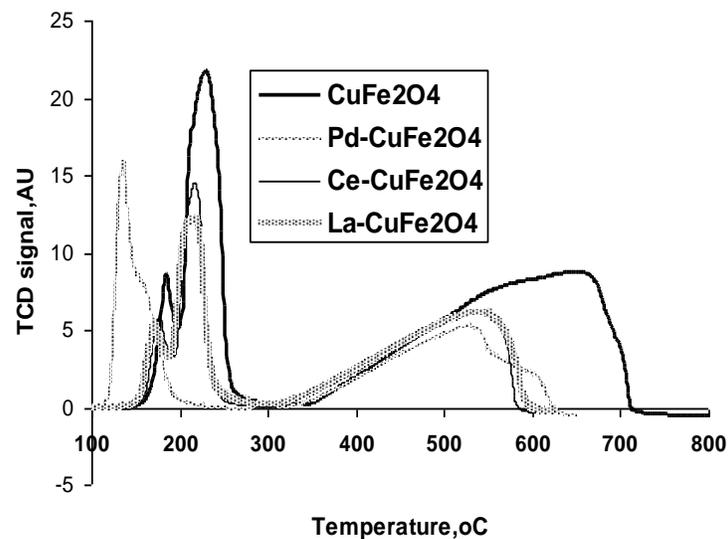


Figure 3(c): TPR profiles of pure and Pd/Ce/La CuFe₂O₄ calcined at 300°C

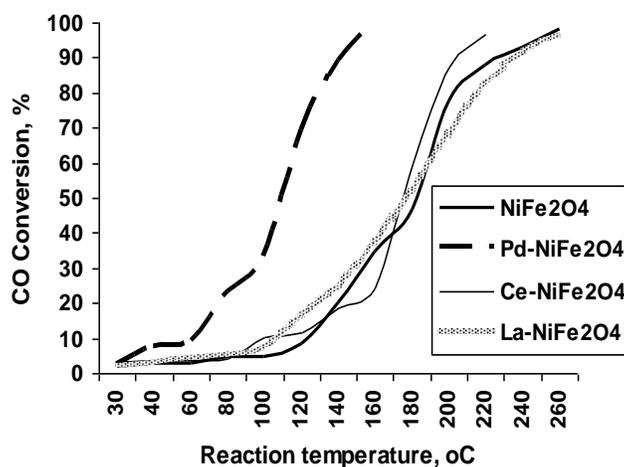


Figure 4(a): CO oxidation profiles of pure and Pd/Ce/La doped NiFe_2O_4 calcined at 300°C

All Palladium impregnated samples showed significant improvement in their performance. Even though La incorporation facilitated the shifting of pore diameter towards the lower pore size region thereby causing an increase in surface area, the catalytic effect on oxidation was not pronounced. Ceria containing samples showed practically no improvement on the oxidation rates. The reduction profiles of most of the Ce and La doped samples are very similar to their parent ferrite samples; a few exceptions are there as in the case of CoFe_2O_4 up on Ce impregnation.

The Pd doped samples showed abrupt difference in their reduction pathway. In the case of NiFe_2O_4 impregnated with 0.3% Pd, the first T_{max} got shifted to 307°C from 429°C . The shifting of the temperature to the lower side by about 120°C is quite significant. For pure CoFe_2O_4 , the first T_{max} is at 554°C , whereas it is at 284°C , 513°C and 511°C for Pd, La and Ce doped CoFe_2O_4 respectively. CuFe_2O_4 showed first T_{max} at 229°C , while the Pd, La and Ce analogues have T_{max} points at 135°C , 215°C and 217°C respectively.

In the case of NiFe_2O_4 , Pd doped sample showed significant improvement in CO oxidation conversion, where as Ce and La samples showed a mixed response. On an average, La and Ce samples have similar conversion trends as that of the un-doped NiFe_2O_4 sample over the entire range of temperatures. For example, at 100°C NiFe_2O_4 had only 4.5 % conversion, where as Pd impregnated samples had 32.9 % conversion. In the meantime, Ce and La impregnated NiFe_2O_4 samples have only 10.2 and 6.8 % conversions respectively. Among CoFe_2O_4 series at T_{100} , the un-doped CoFe_2O_4 has 28.5 % conversion; Ce and La had 10.7 and 30.9 % conversions respectively. For Pd- CoFe_2O_4 sample, T_{100} conversion increased to 53.0 % and is correlated to the shift of reduction peaks in the TPR profile. Pure CuFe_2O_4 is having the best conversion compared to pure Ni and Co samples and exhibits almost full conversion at around 180°C . Upon Pd doping, the conversion at T_{100} came up to 37.5 % from 17.4% of the un-doped samples. Generally in all the cases, Pd doping enhanced the low temperature oxidation in the case of NiFe_2O_4 , CoFe_2O_4 and CuFe_2O_4 samples which would help in the modification of kick-off temperatures of the catalyst samples for exhaust treatment applications.

Doping with Pd gave a prominent enhancement for the reduction of the divalent metals as well as the hematite to magnetite reduction part as observed in the H_2 -TPR pattern. The hydrogen spillover from palladium to the base metal oxide is also likely [12, 14]. It is well known that palladium oxide can be easily reduced to metallic Pd by H_2 . Metallic Pd, as a noble metal shows intrinsically high capability for hydrogen dissociation, which serve as a catalyst triggering the reduction of the other surrounding oxides by dissociating hydrogen molecule with a decrease of activation energy. This amounts to auto catalysis of the gas-solid reaction attributed to hydrogen spillover effect. The H_2 consumption values calculated from the peak area upon calibrated TCD exceeded that required for the Pd or the divalent metal alone or its combination, showing also the occurrence of hematite to magnetite reduction along with.

It is established that CO preferentially gets adsorbed on to noble metals like Pd compared to pure base metal oxides. The spillover of CO from Pd to base metal oxides to consume lattice oxygen is the potential reason for their enhanced catalytic properties. The redox properties of the base metal oxides are also significant. The modification by promoter addition facilitates enhancement in their catalytic activity because the redox properties of the base metal oxides are improved that ease the supply of lattice oxygen for CO oxidation.

The TPR results of Pd containing samples show exactly the kind of reduction pathway that begin at lower temperatures with extension to high temperatures [18, 20]. Even CuFe_2O_4 , the catalyst with best reducibility got

enhanced in their reducibility and activity upon introduction of small amounts of palladium. These results support Mars van Krevelen mechanism that considers redox nature of the catalyst surface as the key parameter for CO oxidation reactions. CO and O₂ compete to get adsorbed on pure base metal oxides at least during the rejuvenation step as discussed in Mars van Krevelen mechanism. Once a CO molecule is adsorbed on a surface, it suppresses the adsorption of O₂ to complete the reaction cycle by filling up the lattice oxygen vacancy. In Pd promoted surfaces, CO preferentially gets adsorbed on Pd allowing O₂ to easily interact with reduced base metal surfaces that enhances the reaction rate even at low temperature. Thus the noble metal incorporated ferrites have very important applications as CO oxidation catalysts.

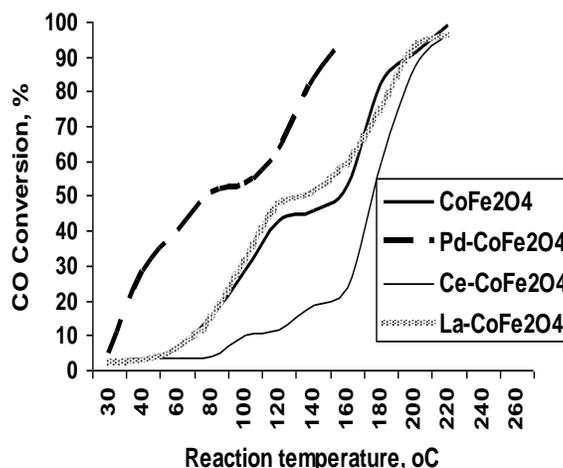


Figure 4(b): CO oxidation profiles of pure and Pd/Ce/La doped CoFe₂O₄ calcined at 300°C

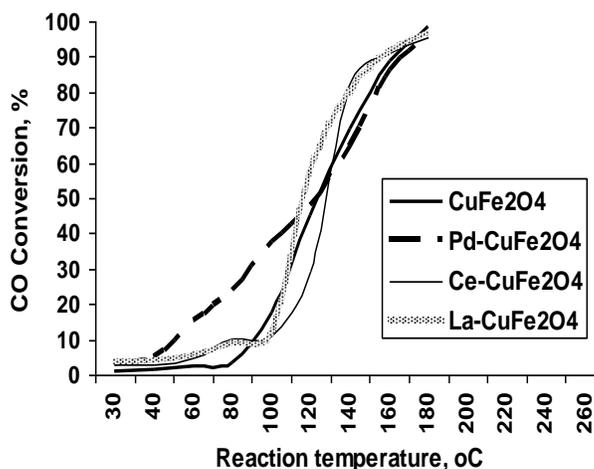


Figure 4(c): CO oxidation profiles of pure and Pd/Ce/La doped CuFe₂O₄ calcined at 300°C.

CONCLUSION

Ferrite catalyst samples are synthesized through methods involving hydrothermal step that directly gives spinel phase. Samples were characterized and the carbon monoxide oxidation activities were evaluated. Promoters like Pd, Ce and La were incorporated via pore filling impregnation method, characterized, and tested for CO oxidation activity. The effect of reducibility of the catalyst precursor and its relation to the CO oxidation especially when Pd is loaded has been investigated. Preferential adsorption of CO compared to oxygen is believed to occur on Pd centers and the lattice oxygen from the base metal oxides steer the formation CO₂. These noble metal loaded catalysts exhibit a strong synergy between the different metal components and thereby acquire enhanced catalytic properties.

REFERENCES

1. Lingaiah N, Babu NS, Rajesh Gopinath, Siva Sankara Reddy P, Sai Prasad PS. Hydrodechlorination of chlorobenzene over supported metal catalysts. *Catal Surv Asia*. 2006;10:1.

2. Huaqing Z, Qin Z, Wenjuan S, Jianguo Wang. Pd/CeO₂-TiO₂ catalyst for CO oxidation at low temperature: a TPR study with H₂ and CO as reducing agents. *J Catal.* 2004; 225:267-277.
3. Santra AK, Goodman DW. Catalytic oxidation of CO by platinum group metals: from ultrahigh vacuum to elevated pressures. *Electrochim Acta.* 2002; 47:3595-3609.
4. Urda A, Herraiz A, Rédey A, Marcu IC. Co and Ni ferros spinels as Catalysts for Propane Total Oxidation, *Catalysis Communications.* Catal Commun. 2009; 10:1651.
5. Silva JB, Diniz CF, Lago RM, Nelcy DS Mohallem. Catalytic properties of nano composites based on cobalt ferrites dispersed in sol-gel silica. *J Non-Cryst Solids.* 2004;348:201.
6. Fouad OA, Abdel Halim KS, Rashad MM. Catalytic Oxidation of CO over Synthesized Nickel Ferrite Nano particles from Fly Ash. *Top Catal.* 2008 ; 47 :61.
7. Kugai J, Miller JT, Guo N, Song C. Oxygen-enhanced Water Gas Shift on Ceria-supported Pd-Cu and Pt-Cu Bimetallic Catalysts. *J Catal.* 2011; 277 :46-53.
8. Mierczynski P, Maniecki TP, Maniukiewicz W, Jozwiak WK. Cu/Cr₂O₃-3Al₂O₃ and Au-Cu/Cr₂O₃-3Al₂O₃ catalysts for methanol synthesis and water gas shift reactions. *Reac Kinet Mech Cat.* 2011;104 :139-148.
9. Fernández-García M, Martínez-Arias A, Iglesias-Juez A, Hungría AB, Anderson JA, Conesa JC, Soria J. Behaviour of bimetallic Pd-Cr/Al₂O₃ and Pd-Cr/(Ce,Zr)O_x/Al₂O₃ catalysts for CO and NO elimination. *J Catal.* 2003; 214:220.
10. Hungría AB, Iglesias-Juez A, Martínez-Arias A, Fernández-García M, Anderson JA, Conesa JC, Soria J. Effects of copper on the catalytic properties of bimetallic Pd-Cu/(Ce,Zr)O_x/Al₂O₃ and Pd-Cu/(Ce,Zr)O_x catalysts for CO and NO elimination. *J Catal.* 2002; 206:281.
11. Mergler YJ, Van Aalst A, Van Delft J, Nieuwenhuys BE. CO oxidation over promoted Pt catalysts. *Appl Catal B-Environ.* 1996; 10:245.
12. Meng M, Zha YQ, Luo JY, Hu TD, Xie TD, Liu T, Zhang T. A Study on the Catalytic Synergy Effect between Noble Metals and Cobalt Phases in Ce-Al-O Supported Catalysts. *Appl Catal A.* 2006; 301:145.
13. Kulshreshtha SK, Gadgil MM. Physico-chemical characteristics and CO oxidation studies over Pd/(Mn₂O₃ + SnO₂) catalyst. *Appl Catal B.* 1997 ; 11:291.
14. Jin-Yong Luo, Ming Meng, Xiang Li, Xin-Gang Li, Yu-Qing Zha, Tian-Dou Hu, et al. Mesoporous Co₃O₄-CeO₂ and Pd/Co₃O₄-CeO₂ catalysts: Synthesis, characterization and mechanistic study of their catalytic properties for low-temperature CO oxidation. *J Catal.* 2008 ; 254 :310-324.
15. Skoglundh M, Johansson H, Lijwendahl L, Jansson K, Dahl L, Hirschauer B. Cobalt-promoted palladium as a three-way catalyst. *Appl Catal B-Environ.* 1996 ; 7 :299-319.
16. Mars P, Van Krevelen DW. Oxidations carried out by means of vanadium oxide catalysts. *Chem Eng Sci Spec suppl.* 1954; 3:41.
17. Ching-Shiun Chen, Jiann-Hwa You, Jarrn-Horng Lin, Chi-Ruei Chen, Keng-Min Lin. Cu/ZnO/Al₂O₃ catalyst for CO oxidation. *Catal Commun.* 2008; 9:1230-1234.
18. Lei Qia, Qiang Yua, Yue Daia, Changjin Tanga, Lianjun Liua, Hongliang Zhanga, et al. Influence of cerium precursors on the structure and reducibility of mesoporous CuO-CeO₂ catalysts for CO oxidation. *Appl Catal B Environ.* 2012;119: 308- 320.
19. Pawel Mierczynski, Piotr Kaczorowski, Tomasz PM, Katarzyna BO, Waldemar Maniukiewicz. The influence of Pd loading on the physicochemical properties of the Cu-Cr-Al methanol synthesis catalysts. *Reac Kinet Mech Cat,* 2013; 109: 13-27.
20. Jin-Yong Luo, Ming Meng, Jin-Song Yao, Xin-Gang Li, Yu-Qing Zha, Xitao Wang, et al. One-step synthesis of nano structured Pd-doped mixed oxides MO_x-CeO₂ (M = Mn, Fe, Co, Ni, Cu) for efficient CO and C₃H₈ total oxidation. *Appl Catal B-Environ.* 2009; 87: 92-103.
21. Aniz CU, Radhakrishnan Nair TD. A study on Catalysis by ferros spinels for preventing atmospheric pollution from carbon monoxide. *Open Journal of Physical Chemistry.* 2011; 1:124-130.
22. Malet P, Caballero A. The selection of experimental conditions in temperature-programmed reduction experiments. *J Chem Soc Faraday Trans.* 1988; 84: 2369-2375.
23. Weisz PB, Prater CD. Interpretation of Measurements in Experimental Catalysis. *Adv Catal.* 1954; 6: 143-196.
24. Aniz CU, Robinson PP, Abdul Rashid KK, Radhakrishnan Nair TD. Correlation between the reduction behavior of ferros spinels synthesized by a soft chemical method and their carbon monoxide oxidation activity. *Reac Kinet Mech Cat.* 2012; 107: 355-365.
25. Yur'eva TM, Boreskov GK, Zharkov VI, Karakchivev LG, Popovskii VV, Chigrina VA. *Kinet Katal.* 1968; 9: 1063.
26. Ramankutty CG, Sugunan S, Bejoy T. Study of cyclohexanol decomposition reaction over the ferros spinels, A_{1-x}Cu_xFe₂O₄ (A = Ni or Co and x = 0, 0.3, 0.5, 0.7 and 1), prepared by 'soft' chemical methods. *J Mol Catal A Chem.* 2002;187: 105-117.