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High catalytic activity of Pt–Pd containing USY zeolite catalyst for low temperature CO oxidation from industrial off gases

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ABSTRACT

Small amounts (0.15wt%) of platinum and palladium were incorporated in porous, high surface area, ultra–stable H–USY–Zeolite by ion exchange method, and their catalytic activity was studied for carbon monoxide (CO) oxidation reaction, under various conditions of industrial importance. The catalyst was characterized by p–XRD, chemical analysis, SEM, TEM, evaluated for catalytic activity using a steady state, fixed bed catalytic reactor. The catalysts show high CO oxidation activity and it was possible to convert 0.044 mmols of CO per gram of catalyst at 120 °C, at a space velocity of 60 000 h^{-1} and with 100 ppm CO concentration in feed gas. The high catalytic activity of this noble metal catalyst also appears to be a factor of porous structure of zeolite facilitating mass transfer; high surface area as well as highly dispersed catalyst sites of palladium and platinum on zeolite structure. Introduction of acidic sites in zeolites probably makes them more resistant towards SO$_2$, while their surface area and pore characteristics make this catalyst efficient even under high space velocity conditions, thus suggesting the potential of larger pore size zeolites over conventional porous materials for industrial applications.

Keywords: Zeolite, catalyst, CO oxidation, nano–catalyst, porous catalyst, off gas treatment

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1. Introduction

Carbon monoxide (CO) is one of the major pollutants emitted from vehicular exhausts, industrial off gases, solid fuel combustion and a variety of other sources. Outstanding progress has been made in development of CO oxidation catalysts, and CO emissions have been very effectively controlled from automobiles by using such catalyst technologies. Most of these catalysts however, use noble metals supported on γ–alumina, with few exceptions of using titania, zirconia, ceria and other oxides as supports (Xu et al., 2006; Ramesh et al., 2008; Chauhan, 2010; Zhang et al., 2011). However, catalytic CO oxidation has always been a subject of great interest, with respect to lowering of noble metal content as well as improving their low temperature activity and stability. This is of particular interest for certain industrial applications, where off–gas contains catalyst poisons like sulfur dioxide (SO$_2$) and carbonyl sulfide (COS). Although, these poisonous gases are effectively removed with the use of scrubbers, this often results in substantial lowering of off–gas temperature, making the catalyst application difficult. Therefore, low temperature activity, affectivity under high space velocity conditions and chemical stability with lower concentrations of poisonous gases are still the major driving forces for the search of new catalyst compositions for industrial applications. The catalytic oxidation of CO at low temperatures is an interesting reaction when the feed composition involves other poisonous gases, which can have considerable impacts on catalytic activity. Stark and co–authors (Stark and Harris, 1983; Stark et al., 1983; Stark and Harris 1988) reported that Pt/SnO$_X$ is an effective catalyst for the oxidation of CO, however, very few reports are available on the effect of other pollutants on the catalytic activity (Thormahlen et al., 1999). It has also been observed in many other

studies that platinum–support interaction affects the activity of platinum catalysts (Wang et al., 2003; Sobczak et al., 2005).

Catalytic activity of material depends upon both chemical and physical properties, such as intrinsic catalytic activity and crucially on the porosity, pore structure or architecture, as well as micro surface area. Hence many efforts were focused on exploring the porous catalyst supports with suitable pore size and surface area. Although, CO oxidation is a relatively simple reaction involving small molecules, the properties of catalyst support becomes important at higher space velocities and in presence of co–existing gases (Aguila et al., 2008; Doggali et al., 2011). Therefore, exploring different porous catalyst supports is of prime academic and practical importance. Zeolites are recognized as one of the most fascinating group of porous materials, which have revolutionized the field of porous materials with precisely controlled porous architecture, leading to a variety of shape selectivity and other related applications (Qiao et al., 2014). Despite these extraordinary properties, zeolites have so far found limited applications in catalytic control of industrial and automobile off–gases. However, substantial improvement with respect to their hydrothermal stability now made them potential candidates for certain industrial applications (Ribeiro et al.,2007; Li et al., 2011), while there are numerous reports coming for their applications in automobile exhaust purification as well (Nejar and Illan–Gomez, 2007; Hasna, 2009). The pore size of zeolites can be selected by selecting Zeolite with appropriate pore diameter (0.2–0.8 nm and even larger), which can further be manipulated by exchanging with cations of different size (Tuan et al., 1999; Labhsetwar et al., 2007). One of the major challenges with zeolites as catalyst supports for environ-mental applications has been their thermal and hydro-thermal

stability, which are rather moderate for most of the zeolites, until the development of highly siliceous zeolites including those Ultrastable Y Zeolite (USY) and Zeolite Socony Mobil–5 (ZSM) types. Nevertheless, many of these zeolites are very suitable for industrial off–gas applications with moderate temperatures in the range of 100–300 °C (Dyakonov, 2003; Silva et al., 2010; Chen et al., 2013).

In the present study, Pt and Pd incorporated H–USY–Zeolite has been synthesized by ion–exchange method and their catalytic activity has been studied in detail for low temperature CO oxidation, considering various requirements for possible industrial applications.

2. Experimental

2.1. Synthesis of catalyst

Pt and Pd incorporation on H–USY zeolite support was done using a combined ion–exchange–impregnation method. Palladium chloride and platinum chloride were taken in appropriate amount with respect to their targeted metal contents and dissolved in requisite quantity of deionized water. Desired amount of H–USY was suspended in deionized water, which was then added to mixed palladium and platinum chloride solution. The resulting mixture was kept in an incubator shaker for 24 h at 150 rpm and the temperature was maintained at 30 °C. The solution afterwards was dried at 60 °C with continuous stirring on hot plate. The resultant material was calcined at 400 °C for 6 h and subsequently reduced in hydrogen atmosphere at 350 °C. The amount of Pt and Pd was optimized after performing experiments with various amounts of noble metals and screening of these catalysts for their catalytic activity.

2.2. Characterization of catalyst

The selected catalyst samples were characterized for chemical composition using inductively coupled plasma atomic emission spectroscopy (ICP–AES) technique after acid digestion of samples. To aid the vaporization of all the atoms in the plasma equally, the samples were acid digested. In a typical protocol for acid digestion, as recommended for ICP–AES analysis, 0.1–0.5 g of catalyst sample was digested with 109.5 mL of ultrapure concentrated nitric acid over the period of a few hours. After this 0.5 mL of the digested solution is placed in 9.5 mL (or more depending on metal concentration) of ultrapure water, and the sample thus obtained was used for analysis. If the samples are not digested using a strong acid to bring the metals atoms into solution, the form of the particle could hinder some of the material being vaporized. The detection of the analyte will be difficult even if it is present in the sample which will lead to inaccurate results. It also helps in removing the protective layer of organic ligands covering nanoparticles. Powder X–ray diffraction (XRD) data were recorded at room temperature on a Rigaku Rint–2 200HF machine, using Bragg–Brentano geometry with CuKα (copper K alpha source) radiations. CuKXRD data were mainly analyzed for presence of Pt and Pd as well as for structural damage if any to zeolite framework during the catalyst preparations. The morphology of the catalyst was studied by Scanning Electron Microscopy (SEM) using JEOL, JXA–840 A, electron probe microanalyser. The morphological and structural details of the catalysts were studied by high resolution transmission electron microscopy (HR–TEM) and was carried out on a JEOL JEM–3010 microscope operated at 300 kV (LaB$_6$ cathode, point resolution 1.7 A). Electron diffraction patterns were evaluated using the Process–Diffraction software package. Sample was dispersed in ethanol and treated in ultrasound for 10 minutes. A drop of very dilute suspension was placed on a holey–carbon–coated copper grid and allowed to dry by evaporation at ambient temperature. Brunauer Emmett Teller (BET) surface area of samples was determined following the standard nitrogen adsorption method using Micromeritics ASAP–200 instrument. Thermal stability experiments were performed by Thermogravimetry (TG) technique, using Rigaku–TAS–200, Thermal Analyzer. Although, both zeolite and noble metals are thermally very stable, TG experiments were performed to study any weight loss or exo/endotherms indicating structural changes in zeolite.

2.3. Catalytic activity evaluations

The catalytic activity for CO oxidation of catalysts was evaluated using an automated, steady state, fixed–bed type catalyst evaluation set–up with quartz catalytic reactors (Figure 1). The experiments were performed at slightly positive pressure of approximately 1.1 bar. The catalyst bed of 100 mg catalyst in powder or bead form was supported by a layer of ceramic wool, and the temperature was maintained with the aid of a PID temperature controlled furnace (ATS, USA). The experimental set up consisted of mass flow controllers (MFC) of Alborg, USA make, and a mixing chamber for simulating an off–gas mixture. The simulated gas mixture containing 500, 1 000, 2 000 ppm CO, 10 vol% O$_2$ balance by helium was used with controllable flow rates of 30–100 SCCM (standard cubic centimeters per minute). Experiments were also performed at different space velocities, especially at higher space velocity, which is quite sufficient for industrial applications. The effluent stream was continuously analyzed by using a Shimadzu gas chromatograph equipped with a thermal conductivity detector (TCD) and 5 A molecular sieve column as well as Porapak–Q column. The catalyst was pre–treated in helium flow at 200 °C for a period of 30 min to remove any volatile contaminant and adsorbed gases. The catalytic activity was evaluated in terms of % conversion (X) of CO gas to CO$_2$ according to the following equation:

$$X_{CO}=(P_{CO\ in}-P_{CO\ out})/P_{CO\ in}\text{x}100 \tag{1}$$

where, $P_{CO\ in}$ is the quantity of CO going in the catalytic reactor and $P_{CO\ out}$ is the quantity of CO coming out of the catalytic reactor.
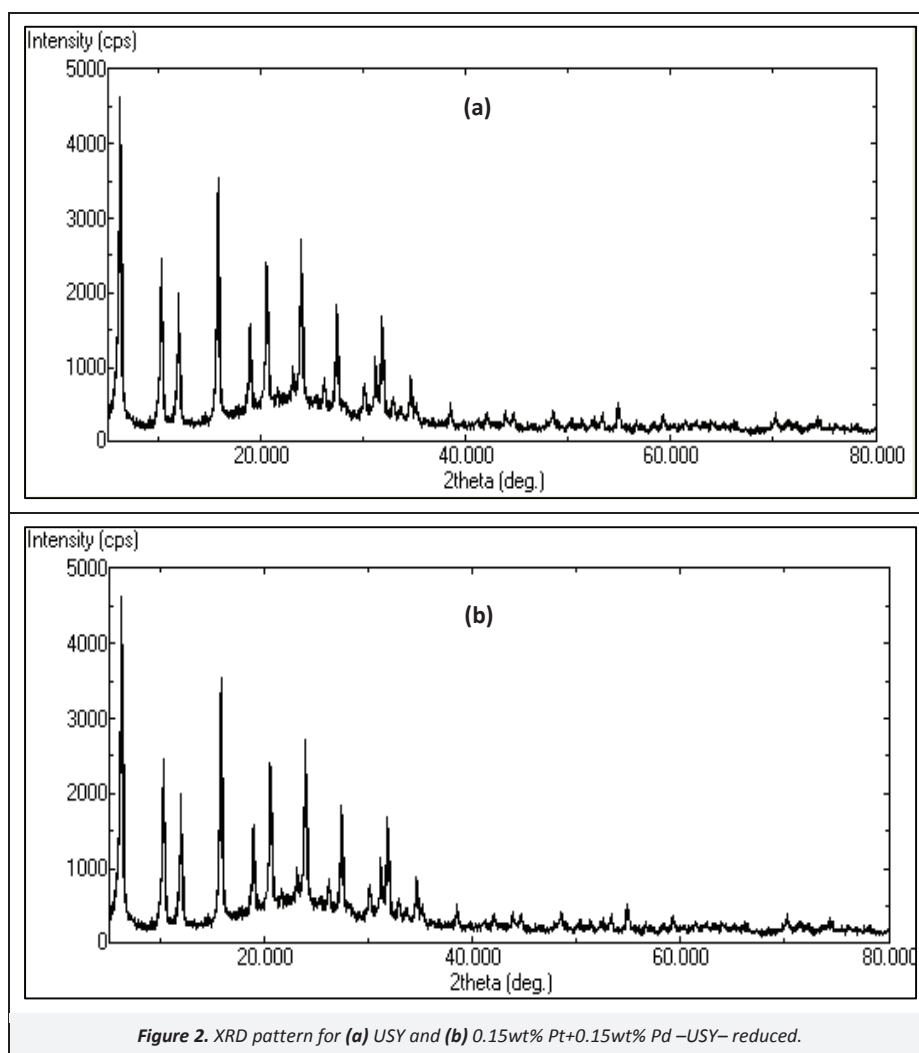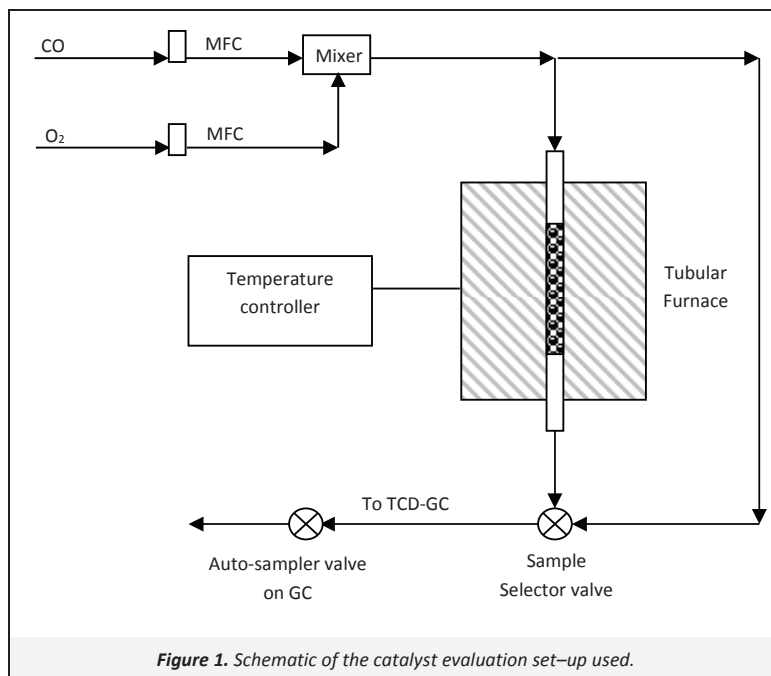
Repeated evaluations were carried out to check the reproducibility of results under various experimental conditions and substantiated with CO/CO$_2$ mass balance.

3. Results and Discussion

3.1. Characterization of catalyst

Powder X–ray diffraction analysis. The powder XRD (*p*XRD) patterns of H–USY and 0.15wt% Pt+0.15wt% Pd–USY–reduced (Pt–Pd–USY) have been recorded to study the effect of metal loading as well as ion exchange treatment on H–USY structure. The XRD patterns match well with the Joint Committee on Powder Diffraction Standards (JCPDS) database (JCPDS card number 12 0246) and therefore confirm the intact USY phase after the ion–exchange experiments. *p*XRD pattern of H–USY (Figure 2a) shows the characteristic crystalline peaks for zeolite–Y structure, while *p*XRD pattern of Pt–Pd–USY (Figure 2b) also shows characteristic crystalline diffraction peaks similar to that of USY. It was not possible to identify the presence of Pt and Pd due to their low content and high dispersion. There was practically no change observed in the *d*–spacing values of both the zeolites. This proves that the zeolitic crystalline structure was intact, which was also expected considering the very mild conditions used for Pt/Pd incorporation. The pXRD analysis thus clearly inferred no impact of metal incorporation on zeolite framework under the experimental conditions used.

Scanning electron microscopic (SEM) observations. The morphology of Pt–Pd–USY is revealed by SEM micrographs as shown in Figure 3. As it can be seen from the SEM images of varying magnifications Figure 3a at 5 μm and Figure 3b at 10 μm, Pt–Pd–USY particles exhibit a highly ordered morphology, thereby confirming practically no effect on this zeolite based catalyst after Pt/Pd incorporation.
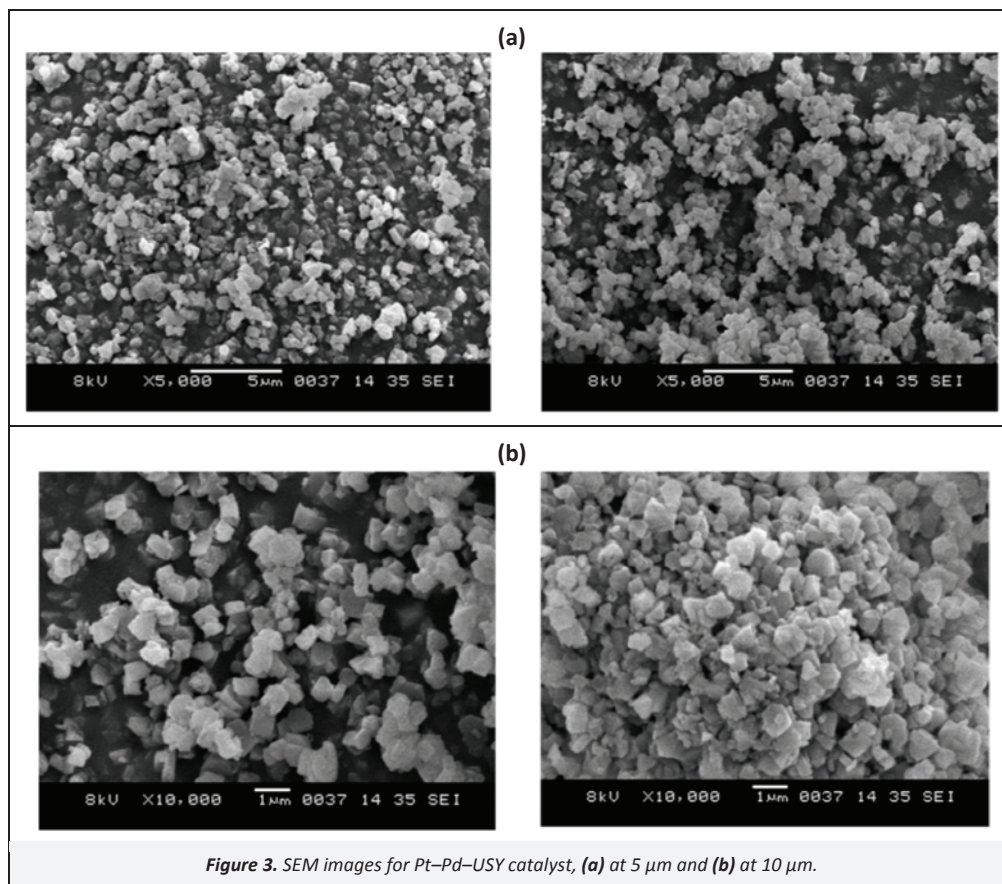
Figure 1. *Schematic of the catalyst evaluation set–up used.*

Figure 2. *XRD pattern for **(a)** USY and **(b)** 0.15wt% Pt+0.15wt% Pd –USY– reduced.*

Figure 3. *SEM images for Pt–Pd–USY catalyst, (a) at 5 µm and (b) at 10 µm.*

Transmission electron microscopy (TEM). The TEM image of Pt–Pd–USY is shown in Figure 4. The catalyst was examined under the TEM for any possible presence of metal on zeolite surface but no traces of such particles were observed thereby suggesting their presence mainly in the zeolite pores presumably on the cation exchange sites, which were difficult to access even with TEM analysis.
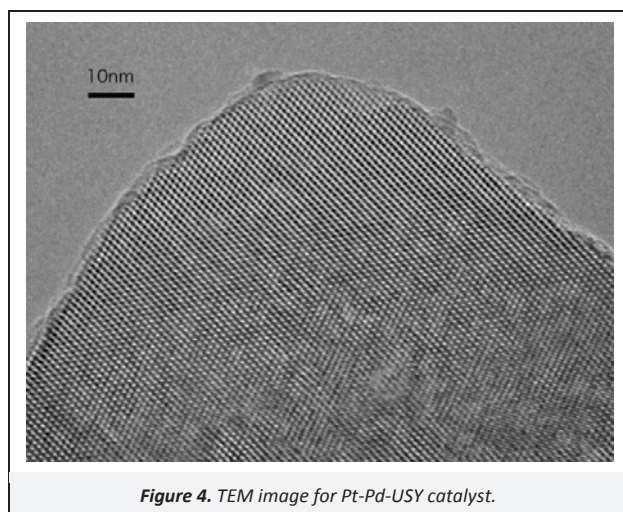

Figure 4. *TEM image for Pt-Pd-USY catalyst.*

Surface area and pore volume. The BET–surface area analysis of this material has been carried out using Micromeritics Adsorption Analyzer. Minor change in specific surface area was observed in the case of Pt/Pd–USY, which is expected considering the incorporation of metals as well as experimental errors. The specific surface area for bare USY support observed was 780 $m^2\,g^{-1}$. While in case of Pt/Pd–USY, the specific surface area was moderately reduced to 684.6 $m^2\,g^{-1}$, with pore volume and pore size values of 0.46522 $cm^3\,g^{-1}$ and 28.86 A respectively. This was determined using nitrogen adsorption technique following BET method. The specific surface area of Pt–Pd–USY catalyst observed was significantly higher than those of alumina based conventional catalysts.

3.2. Catalytic activity measurements

Catalytic activity for CO oxidation. Our recent studies on perovskite based catalysts for CO oxidation reaction show very good catalytic activity, however, most of those perovskite type catalysts possess very low surface area (generally in the range of 1–10 $m^2\,g^{-1}$, as also reported by many researchers) (Ciambelli et al., 2001; Zhang–Steenwinkel et al., 2002; Singh et al., 2007). Therefore, such catalysts may not be very suitable for high space velocity applications (Chen et al., 2013), which is typically observed in several industrial as well as auto–exhaust applications. This is due to the high temperature requirement for perovskite synthesis, which results in formation of sintered phase with very low surface area. This has been a major limitation with perovskite type catalysts, which are otherwise low cost options due to the use of common transition metals. A large number of publications are reported on zeolite based CO oxidation catalysts, however, most of the recent work was focused on PROX reaction for fuel cell application. The USY with excellent hydrothermal stability and low cost, offers a potential catalyst support for industrial off–gas applications with moderate temperature. The catalytic activity results for CO oxidation as a function of temperature are shown in Figure 5. Under the reaction conditions using a gas mixture containing CO=500 ppm+O_2=12% and balance He, with a space velocity of approximately 40 000 h^{-1}, the catalyst shows high

activity for CO oxidation. To be more precise, the catalyst became active around 80 °C (presumably light–off temperature) followed by a spur in activity at around 90 °C with 100% CO conversion as observed at around 100 °C. This is good catalytic activity for moderate amount of noble metal loading and using reasonably high space velocity. As use of dry scrubber is quite common for removal of catalyst poisoning gases and other environmental regulated emissions from industrial exhaust, the resulting off gas temperature is usually in the temperature range of 100–200 °C. Such a high catalytic activity at 100 °C is therefore, of significance. The Figure 5 also depicts the effect of CO concentration on catalytic activity. As clear from the results, in case of 1 000 ppm initial CO concentration, the catalyst gets activated at 100 °C with 100% CO conversion observed at 120 °C. This temperature was however, increased to 150 °C for 2 000 ppm initial CO concentration. The present catalyst is therefore effective for such industrial off gas temperature range for industrial CO control. The improved catalytic activity of Pt–Pd–USY catalyst should be mainly due to the higher surface area of the zeolite support as well as high dispersion of metal through ion exchange process used. Such a low temperature oxidation activity could be of practical importance even for many industrial applications, where it is difficult to achieve temperature beyond 150–200 °C e.g. alumina process plants.
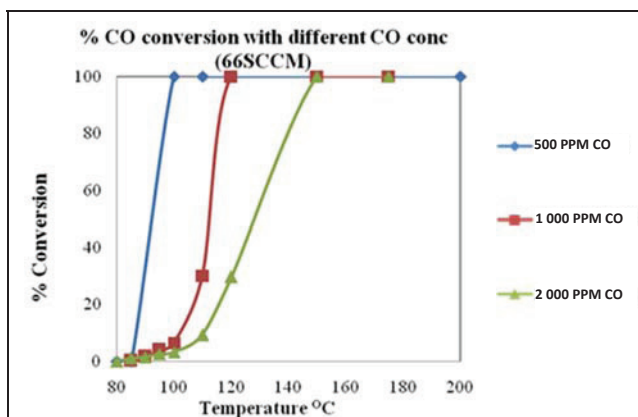

Figure 5. *CO oxidation over0.15wt% Pt+0.15wt% Pd –USY– reduced (Feed composition: CO=500 ppm (blue), 1 000 ppm (red), 2 000 ppm (green), O_2=12% balance He at approximately 40 000 h^{-1} space velocity).*

Effect of space velocity. One of the important parameters for which, many mixed oxide based catalysts fails to achieve desired catalytic activity is the effect of space velocity. Typically industrial off–gases applications are characterized by higher space velocity, in the range of 40 000–60 000 h^{-1}. Owing to this high space velocity range, it becomes very important to study the effect of different space velocities on catalytic activity of the designed catalyst. A set of evaluations has been carried out using different space velocities and with different concentrations of CO. The reason for taking various CO concentrations at different space velocities was clearly to evaluate potential of catalyst for off–gas application, where both space velocity and CO concentrations are varied quite frequently. Such study also helps to decide the volume of catalyst required for the particular flow of off–gas and targeted control of CO to meet the legislative requirements. This always has direct bearing on the cost of catalyst application. The catalyst was subjected to feed gas flow of 100 SCCM, 66 SCCM and 33 SCCM, using a catalyst amount of 100 mg, thus corresponding to gas hourly space velocity of approximately 60 000 h^{-1}, 40 000 h^{-1} and 20 000 h^{-1} respectively. The feed gas composition was containing different concentrations of CO, e.g. 500 ppm, 1 000 ppm and 2 000 ppm.

As expected, there is a gradual decrease in activity of catalyst with increase in space velocity. However, this decrease in catalytic

activity was observed to be marginal at space velocity of 60 000 h^{-1} as shown in Figure 6. The catalyst shows 100 % CO conversion (T$_{100}$) at 100 °C for initial CO concentration of 500 ppm, while this temperature T$_{100}$ was increased to 150 °C for concentration of 2 000 ppm. The reaction seems to be still in kinetic regime only, especially for the CO concentrations of 500 and 1 000 ppm. This is mainly because of the very high surface area as well as ordered, highly porous structure of zeolite support, facilitating mass transfer. The present study therefore, infers that zeolites with reasonable pore size can be very useful catalyst support, especially for the reactions involving relatively smaller molecules like CO, as in the present case. As explained by Dyakonov (2003), zeolite pores up to 4 A do not show significant carbon monoxide adsorption and thus mass transfer can be restricted on such zeolitic supports. Adsorptive retention is also reported to increase dramatically at 5 A aperture. This is obviously because the effective diameter of a CO molecule is approximately 4.5 A. In this way, the USY type zeolite used in the present case is quite suitable for the mass transfer of reactants on catalyst sites, thereby showing effective catalytic activity even at higher space velocity.
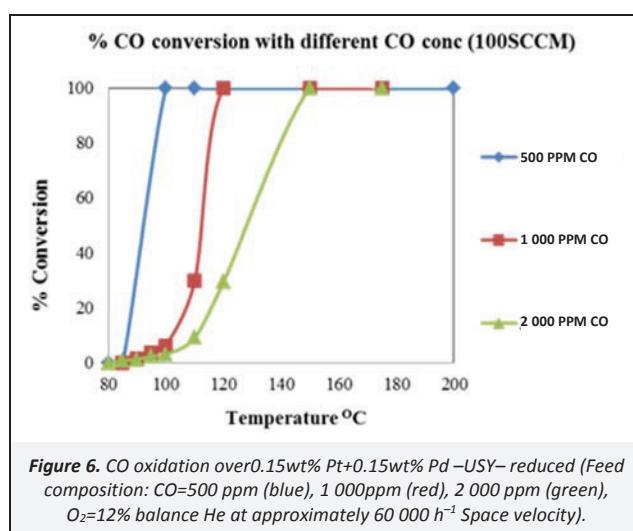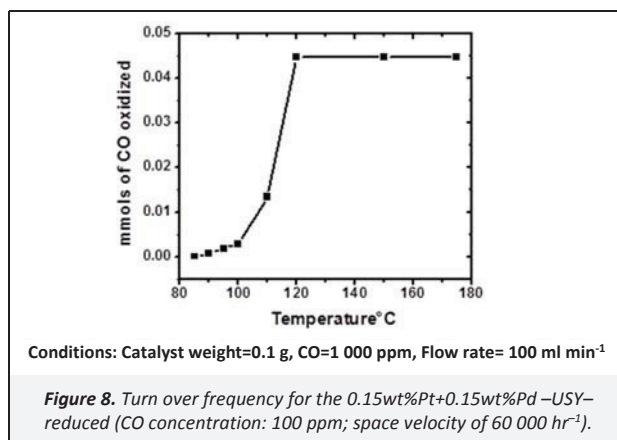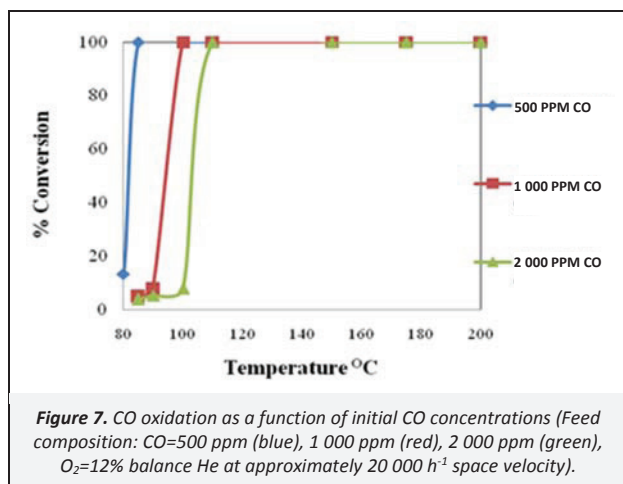

Figure 6. *CO oxidation over0.15wt% Pt+0.15wt% Pd –USY– reduced (Feed composition: CO=500 ppm (blue), 1 000ppm (red), 2 000 ppm (green), O_2=12% balance He at approximately 60 000 h^{-1} Space velocity).*

Figure 7 provides the results for catalytic CO oxidation at a space velocity of 20 000 h^{-1}. It is clear from the results that the catalyst gets activated at about 80 °C, and immediately attends T$_{100}$ even below 90 °C for initial CO concentration of 500 ppm. The activity was also very high for higher initial CO concentrations of 1 000 and 2 000 ppm with T$_{100}$ observed at 100 and 110 °C respectively. The catalyst works in kinetic regime, and the well dispersed catalyst sites on porous zeolite support offers this high activity for CO oxidation. The catalyst was subjected to 24 h of continuous exposure in the feed gas at 120 °C and does not show any significant impact on CO oxidation activity.

Figure 8 shows the Turn Over Frequency (TOF) for the 0.15wt% Pt+0.15wt %Pd–USY catalyst studied for catalytic CO oxidation reaction. TOF was calculated as mmol of CO converted per gram of catalyst per unit time. Maximum 0.044 mmol CO conversion per gram of catalyst was observed at 120 °C for the present catalyst, which is quite high considering the temperature used. This suggests the high intrinsic activity of catalyst, and thus justifies the use of noble metal at low amount. Such a high TOF values also indicate towards excellent dispersion of catalytic sites and efficient mass transfer on the catalyst.
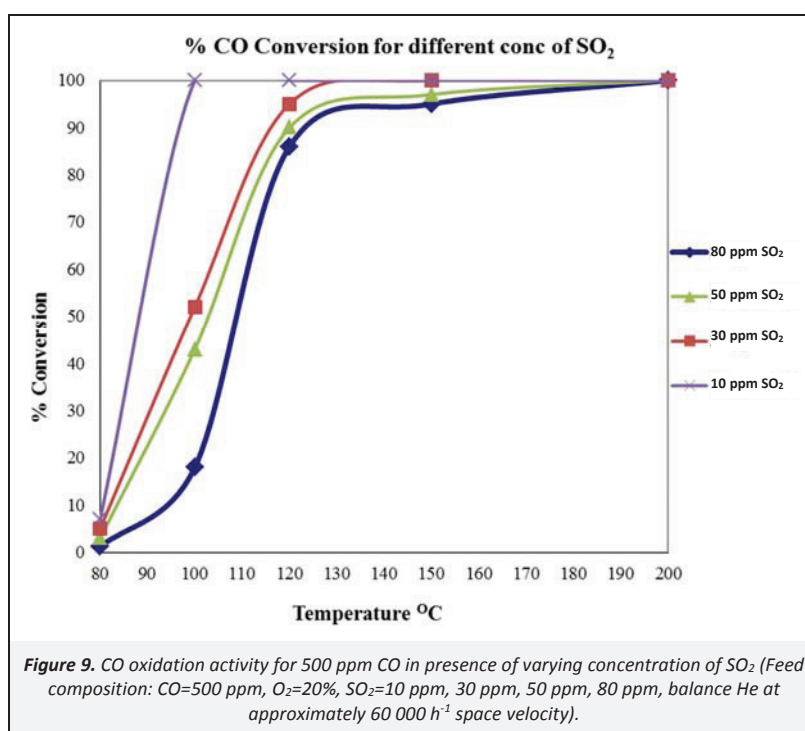
Effect of SO₂ on the catalytic activity. The off–gas from industrial production facilities does contain poisonous gases, such as SO₂, which can have potential detrimental effect on catalytic activity. Therefore, Pt+Pd–USY catalyst was subjected to short term poisoning study to investigate, whether these catalysts show

desired activity in presence of such poisonous components. The catalyst was subjected to 500 ppm of CO with varying concentrations of SO_2 at a space velocity of 60 000 h^{-1} to understand the deteriorating effect of SO_2. As can be seen in Figure 9, practically no effect of SO_2 was observed for a low SO_2 concentration of 10 ppm. However, the impact of SO_2 could be clearly demonstrated for higher concentration and there was significant increase in temperature for CO oxidation activity. The catalyst, however, shows more than 85% CO conversion beyond 120 °C, even in presence of 80 ppm of SO_2. Although, more detailed studies are required to assess the stability of catalytic activity in presence of SO_2, these preliminary results suggest the moderate resistance of catalyst for SO_2. This could be due to the presence of acidic sites in H–USY zeolite support, which does not attract the acidic SO_2 molecules. Pt–Pd based USY zeolites are also reported to show improved sulfur tolerance for catalytic hydrogenation reaction (Mochizuki et al., 2008), thus substantiating the hypothesis. The activity observed for the present catalyst in a temperature window is suitable for application of dry scrubbing of poisonous gases like SO_2, which typically reduces the off gas temperature to about 100–150 °C, with residual SO_2 concentration of as low as 10 ppm.

Conditions: Catalyst weight=0.1 g, CO=1 000 ppm, Flow rate= 100 ml min⁻¹

Figure 8. Turn over frequency for the 0.15wt%Pt+0.15wt%Pd –USY–reduced (CO concentration: 100 ppm; space velocity of 60 000 hr⁻¹).

4. Conclusions

With ever increasing demand of catalysts for industrial and environmental applications, it is of prime importance to search for improved supports for a variety of reactions. The high activity of catalyst is also of prime importance, which effectively reduces the amount of expensive catalyst. Considering the increasing cost of noble metal based catalysts for environmental applications, as well as their limited availability, it is of utmost importance to develop new catalysts with improved catalytic activity under the conditions of practical relevance. High surface area zeolites with microporous structure of precise pore architecture possess desired qualities to be used as a catalyst support. The USY type zeolite with its relatively higher pore size and improved hydrothermal stability is a potential candidate for use as a catalyst support for industrial emission control, as demonstrated in the present work. The catalyst is synthesized using ion exchange method, which is an efficient, easy and relatively green synthesis process for the preparation of metal incorporated zeolites. The process used for the preparation of catalyst is also simple to upscale for industrial applications. CO is one of the most important pollutants emitted from automobiles as well as industrial sources, and continued

Figure 7. CO oxidation as a function of initial CO concentrations (Feed composition: CO=500 ppm (blue), 1 000 ppm (red), 2 000 ppm (green), O₂=12% balance He at approximately 20 000 h⁻¹ space velocity).

Figure 9. CO oxidation activity for 500 ppm CO in presence of varying concentration of SO₂ (Feed composition: CO=500 ppm, O₂=20%, SO₂=10 ppm, 30 ppm, 50 ppm, 80 ppm, balance He at approximately 60 000 h⁻¹ space velocity).

search for improved catalysts with low temperature activity and poison resistance is of importance. The present 0.15wt% Pt+ 0.15wt% Pd –USY catalyst based on an optimized amount of Pt and Pd shows high catalytic activity for CO oxidation at higher space velocity and with higher CO concentrations. 100% CO conversion was observed in a temperature range 90–140 °C, depending on space velocity and initial CO concentrations for present Pt–Pd based USY supported catalyst. It was possible to oxidize 0.044 mmol of CO per gram of catalyst at 120 °C with 100 ppm of initial CO concentration. This should be primarily due to the high surface area and pore structure of zeolite, offering improved mass transfer of reactants. The ion exchange method offers uniform distribution of metal in zeolite channels for their efficient utilization. This is of interest for industrial CO control, where the off gas temperature is often low, because of the use of dry scrubber to remove the poisonous gases like SO_2. The catalyst also shows resistance to SO_2 at lower concentration of 10 ppm for a short exposure, which could be due to its acidic nature. With commercial availability of such zeolites, they present a potential option for their possible application as catalyst support.

Acknowledgments

References

Aguila, G., Gracia, F., Araya, P., 2008. CuO and CeO_2 catalysts supported on Al_2O_3, ZrO_2, and SiO_2 in the oxidation of CO at low temperature. *Applied Catalysis A–General* 343, 16–24.

Chauhan, S., 2010. Noble metal catalysts for monolithic converters. *Journal of Chemical and Pharmaceutical Research* 2, 602–611.

Chen, H.H., Zhang, H.P., Yan, Y., 2013. Catalytic combustion of volatile organic compounds over a structured zeolite membrane reactor. *Industrial & Engineering Chemistry Research* 52, 12819–12826.

Ciambelli, P., Cimino, S., De Rossi, S., Lisi, L., Minelli, G., Porta, P., Russo, G., 2001. $AFeO_3$ (A=La, Nd, Sm) and $LaFe_{1-x}Mg_xO_3$ perovskites as methane combustion and CO oxidation catalysts: Structural, redox and catalytic properties. *Applied Catalysis B–Environmental* 29, 239–250.

Doggali, P., Kusaba, H., Einaga, H., Bensaid, S., Rayalu, S., Teraoka, Y., Labhsetwar, N., 2011. Low–cost catalysts for the control of indoor CO and PM emissions from solid fuel combustion. *Journal of Hazardous Materials* 186, 796–804.

Dyakonov, A.J., 2003. Abatement of CO from relatively simple and complex mixtures – I. Oxidation on Pd–Ag/zeolite. *Applied Catalysis B–Environmental* 45, 241–255.

Hasna, A.M., 2009. Reduction of NO_X gases using copper zeolite catalyst. *Proceedings of the World Congress on Engineering 2009,* July 1–3, 2009, London, UK, pp. 657–661.

Labhsetwar, N., Minamino, H., Mukherjee, M., Mitsuhashi, T., Rayalu, S., Dhakad, M., Haneda, H., Subrt, J., Devotta, S., 2007. Catalytic properties of Ru–mordenite for NO reduction. *Journal of Molecular Catalysis A–Chemical* 261, 213–217.

Li, J.H., Chang, H.Z., Ma, L., Hao, J.M., Yang, R.T., 2011. Low–temperature selective catalytic reduction of NO_X with NH_3 over metal oxide and zeolite catalysts–a review. *Catalysis Today* 175, 147–156.

Mochizuki, T., Toba, M., Morita, Y., Yoshimura, Y., 2008. Effect of loading on aromatic hydrogenation activity of Pd–Pt/USY zeolite catalysts. *Journal of the Japan Petroleum Institute* 51, 58–64.

Nejar, N., Illan–Gomez, M.J., 2007. Noble–free potassium–bimetallic catalysts supported on beta–zeolite for the simultaneous removal of NO_X and soot from simulated diesel exhaust. *Catalysis Today* 119, 262–266.

Qiao, K., Li, X., He, L., Liu, X., Yan, Z., Xing, W., Qin, L., Dai, B., Zhang, Z., 2014. An efficient modification of ultra–stable Y zeolites using citric acid and ammonium fluosilicate. *Applied Petrochemical Research* 4, 373–378.

Ramesh, K., Chen, L., Chen, F., Liu, Y., Wang, Z., Han, Y., 2008. Re–investigating the CO oxidation mechanism over unsupported MnO, Mn_2O_3 and MnO_2 catalysts. *Catalysis Today* 131, 477–482.

Ribeiro, M.F., Silva, J.M., Brimaud, S., Antunes, A.P., Silva, E.R., Fernandes, A., Magnoux, P., Murphy, D.M., 2007. Improvement of toluene catalytic combustion by addition of cesium in copper exchanged zeolites. *Applied Catalysis B–Environmental* 70, 384–392.

Silva, E.R., Silva, J.M., Oliveira, F.A.C., Vaz, M.F., Ribeiro, F., 2010. Cordierite foam supports washcoated with zeolite–based catalysts for volatile organic compounds (VOCs) combustion. *Advanced Materials Forum V, Pt 1 and 2* 636–637, 104–110.

Singh, U.G., Li, J., Bennett, J.W., Rappe, A.M., Seshadri, R., Scott, S.L., 2007. A Pd–doped perovskite catalyst, $BaCe_{1-x}Pd_xO_3$–delta, for CO oxidation. *Journal of Catalysis* 249, 349–358.

Sobczak, I., Ziolek, M., Nowacka, M., 2005. Preparation and characterisation of Pt containing NbMCM–41 mesoporous molecular sieves addressed to catalytic NO reduction by hydrocarbons. *Microporous and Mesoporous Materials* 78, 103–116.

Stark, D.S., Harris, M.R., 1988. The application to sealed CO_2 tea lasers of platinum catalysts bonded to aluminium–containing ferritic steel. *Journal of Physics E–Scientific Instruments* 21, 715–718.

Stark, D.S., Harris, M.R., 1983. Catalyzed recombination of CO and O_2 in sealed CO_2 tea–laser gases at temperatures down to –27–degrees–c. *Journal of Physics E–Scientific Instruments* 16, 492–496.

Stark, D.S., Crocker, A., Steward, G.J., 1983. A sealed 100–Hz CO_2 tea laser using high CO_2 concentrations and ambient–temperature catalysts. *Journal of Physics E–Scientific Instruments* 16, 159–161.

Thormahlen, P., Skoglundh, M., Fridell, E., Andersson, B., 1999. Low–temperature CO oxidation over platinum and cobalt oxide catalysts. *Journal of Catalysis* 188, 300–310.

Tuan, V.A., Falconer, J.L., Nobel, R.D., 1999. Alkali–free ZSM–5 Membranes: Preparation conditions and separation performance. *Industrial & Engineering Chemistry Research* 38, 3635–3646.

Wang, D., Penner, S., Su, D.S., Rupprechter, G., Hayek, K., Schlogl, R., 2003. Silicide formation on a Pt /SiO_2 model catalyst studied by TEM, EELS, and EDXS. *Journal of Catalysis* 219, 434–441.

Xu, R., Wang, X., Wang, D.S., Zhou, K.B., Li, Y.D., 2006. Surface structure effects in nanocrystal MnO_2 and Ag/MnO_2 catalytic oxidation of CO. *Journal of Catalysis* 237, 426–430.

Zhang, Y.X., Su, Q.Y., Li, Q., Wang, Z.P., Gao, X.Y., Zhang, Z.L., 2011. Determination of mechanism for soot oxidation with NO on potassium supported Mg–Al hydrotalcite mixed oxides. *Chemical Engineering & Technology* 34, 1864–1868.

Zhang–Steenwinkel, Y., Beckers, J., Bliek, A., 2002. Surface properties and catalytic performance in CO oxidation of cerium substituted lanthanum–manganese oxides. *Applied Catalysis A–General* 235, 79–92.