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PALLADIUM-SUPPORTED Γ-Al_2O_3 CATALYST VIA HOMOGENEOUS DEPOSITION PRECIPITATION (HDP) METHOD FOR THE REDUCTION OF NO BY CO.

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ABSTRACT

This study investigates the preparation of nanosized palladium (Pd)-supported catalysts for efficient NO reduction by carbon monoxide (CO). Palladium, an alternative to scarce rhodium-based catalysts, was explored due to its potential for enhanced catalytic activity and stability at high temperatures. This study demonstrated two methods of catalyst preparation for NOx reduction: homogeneous deposition precipitation (HDP) and impregnation, where γ-Al_2O_3, Al_2O_3, and SiO_2 are used as supports. The HDP method yielded catalysts with smaller Pd particles (5.2-5.6 nm) compared to those prepared by impregnation (15.2 nm). Characterization using X-ray diffraction (XRD), transmission electron microscopy (TEM), and other techniques confirmed the high dispersion and uniformity of Pd particles on γ-Al_2O_3 supports. The NO-CO reaction's catalytic performance was evaluated. HDP-prepared Pd/γ-Al_2O_3 exhibited superior activity, with NO conversion reaching 100% at 235°C, compared to 310°C for the impregnation method. The study also highlighted the impact of support material, with γ-Al_2O_3 showing better performance than Al_2O_3 and SiO_2. In conclusion, the HDP method is effective for preparing nanosized Pd catalysts with high activity and efficiency for NO reduction. The results indicate that the catalytic performance of NOx reduction applications is significantly improved by the use of smaller Pd particles and optimal support materials.

Keywords: Homogeneous Deposition Precipitation (HDP), Pd-Supported Catalysts, NO Reduction by CO, γ-Al_2O_3 Support, Impregnation Method.

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INTRODUCTION

The diesel engine exhaust contains a lot of NOx compared with gasoline engines. Due to the thermally unstable nature of NOx, it does not undergo a decomposition reaction, showing a high activation energy of about 364 kJ/mol. Hence, a catalyst requires low activation energy to carry out decomposition rapidly. Many effective catalysts based on zeolites have been reported,[1,2] however, Al_2O_3 is used extensively.[3,4] Current three-way catalysts contain Pt + Rh or Pd + Rh supported on alumina and ceria,[5,6] rhodium being the major component due to its low-temperature catalytic activity and high selectivity. Due to the high price and scarcity of rhodium, it is necessary to find an alternative, efficient catalyst with low-temperature activity to reduce NO by CO. NO reduction by CO over supported Pd catalysts has been intensively studied.[7,8] As a result, the NO-CO reaction has been studied over Pd single crystals [11,12] and high-surface-area Pd/Al_2O_3 powder catalysts.[13] Nano-catalysts show better activity due to the availability of a high surface area and density for reaction. Nano-catalysts also exhibit diverse properties like electrical, magnetic, optical, etc., making them more attractive to be used as catalysts. The tiny particle size of palladium shows high catalytic activity; hence, scholars have an opportunity to reduce NO by CO.[14] This allows for the continuous elimination of both NO and CO molecules. A smaller particle size of palladium nano-materials is better for the reduction of NO by the CO reaction. Larger particle size results in the formation of N_2O, in contrast to the higher production of N_2 in the case of smaller particle size. These nano-sized noble metals could serve as better catalysts because of the large surface area and the high density of active sites for NO reduction by CO.

EXPERIMENTAL

Catalyst Preparation

The preparation of γ-Al_2O_3 was typically by $Al(OH)_3$ dissolved in distilled water with constant stirring for 60 min. TEABr (tetraethyl ammonium bromide) was dissolved in distilled water separately and then slowly added to the $Al(OH)_3$ solution. Adjust pH to 5.2 using 1:1 HNO_3. Again, stir for 1 hr. Then transfer this solution to R.B. Flask for reflux at 263 K with constant stirring for 24 hrs. Then filter and dried at 383 K. for 12 hr. Finally, calcined powder at 725 K for 4 hrs.

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The gel composition for γ-Al_2O_3 was Al $(OH)_3$/TEABr/H_2O 1 0.05 50. The synthesis of the Pd/γ-Al_2O_3 catalyst can be carried out by using the HDP method in the presence of urea as a precipitate reagent. The addition of aqueous solution containing 4 wt.% $PdCl_2$ and urea was stirred and heated regularly up to 95°C for a duration of 6 hrs. On decomposition, urea converts into ammonia, and hence, precipitation occurs uniformly by changing the pH into a basic condition. The synthesis of the Pd/γ-Al_2O_3 catalyst can be carried out by using the HDP method in the presence of urea as a precipitate reagent. The addition of aqueous solution containing 4 wt.% $PdCl_2$ and urea was stirred and heated regularly up to 95°C for a duration of 6 hrs. On decomposition, urea converts into ammonia, and hence, precipitation occurs uniformly by changing the pH into a basic condition. The catalyst impPdγ-Al_2O_3 is prepared by the impregnation method.

Determination of Catalytic Activity in the NO-CO Reaction

Feed gases with 1600 ppm CO and 589 ppm NO composition was passed through a mass flow controller with a feed flow rate of 850 ml/min, corresponding to a space velocity of 44000 h^{-1}. The required weight (150 mg) of Pd-supported γ-Al_2O_3, Al_2O_3, and SiO_2 catalysts without any pretreatment was placed inside the catalyst bed, which had a length of 20 mm and a diameter of 8 mm, using quartz wool plugs.

RESULTS AND DISCUSSION

Catalyst Characterization

All the samples were systematically characterized using XRD, N_2 Sorption isotherm, DRUV-VIS spectra, Confocal Raman Spectra, TEM, and ICP-AES techniques. The XRD patterns of the samples under investigation are presented in Fig.-1. The XRD patterns observed for the Al_2O_3, γ-Al_2O_3, and SiO_2 support correspond to their single phase, so the type of noble metal species formed in the catalysts was identified by XRD analysis. The XRD patterns of palladium-supported fresh Pd-Al_2O_3, fresh Pd-γ-Al_2O_3, 3rd time used Pdγ-Al_2O_3, impPdγ-Al_2O_3, and PdSiO_2 used catalysts contain an additional pronounced peak by the PdO phase, with particle sizes of 5.3, 5.2, 5.4, 14.7, and 5.3 nm shown in Fig.-1 (a, b, c, d, e), respectively. The XRD patterns of fresh Pdγ-Al_2O_3 and the 3rd time-used Pdγ-Al_2O_3 catalysts were similar in Fig.-(b), (c), with the same particle sizes of PdO observed. This suggests PdγAl_2O_3 to be a truly thermally stable catalyst, and oligomerization of PdO oxide particles was not observed after the reaction. It shows that the catalyst's nature remains the same after the reaction.

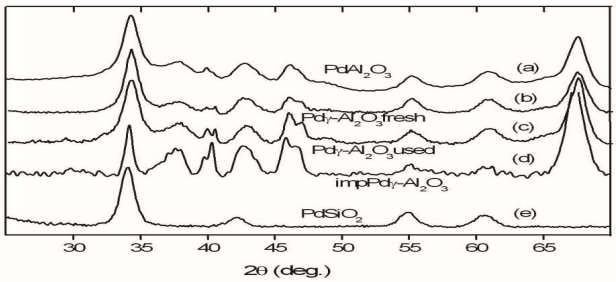

Fig.-1: XRD Patterns of Palladium Supported γ-Al_2O_3, Al_2O_3, and SiO_2 Catalysts

The surface area of all supports was (γ-Al_2O_3 (258 m^2/g), (Al_2O_3 (150 m^2/g), and SiO_2 (190 m^2/g) before metals loading. There was no considerable impact on surface area after palladium loading Table-1 which also indicates the high dispersion of palladium species on exchange sites of the supports. ICP-AES results (reported in Table-1) indicate 100 % loading happened over the support. This indicates a high loading efficiency obtained by the HDP method with the help of a cheap palladium chloride source. Attaining a maximum loading and preventing loss of noble metal is very important for the preparation of supported palladium catalysts for practical usage.

Table-1: XRD, Grain Size, ICP-AES, N_2 Sorption Analysis, and NO Reduction Results for the Various Catalysts

Catalyst	Weight[a] (%)	Grain Size[b](nm)	Surface area(m^2g^{-1})	NO Conversion		
				25%	50%	100%
Pd γ-Al_2O_3	2.94	5.3	212	175°C	190°C	225°C
ImpPdγ-Al_2O_3	2.73	14.7	205	210°C	245°C	310°C
$PdAl_2O_3$	2.95	5.9	130	175°C	190°C	225°C
$PdSiO_2$	2.97	5.3	170	235°C	245°C	280°C

[a]ICP-AES for noble metals contents, [b]particle size was calculated by Scherrer formula.

Figure-2 shows the typical TEM micrographs for the (A) Pdγ-Al_2O_3, (B) $PdSiO_2$, and (C) impPdγ-Al_2O_3 samples, followed by calcination at 450°C. TEM images of palladium loaded on various supports depict

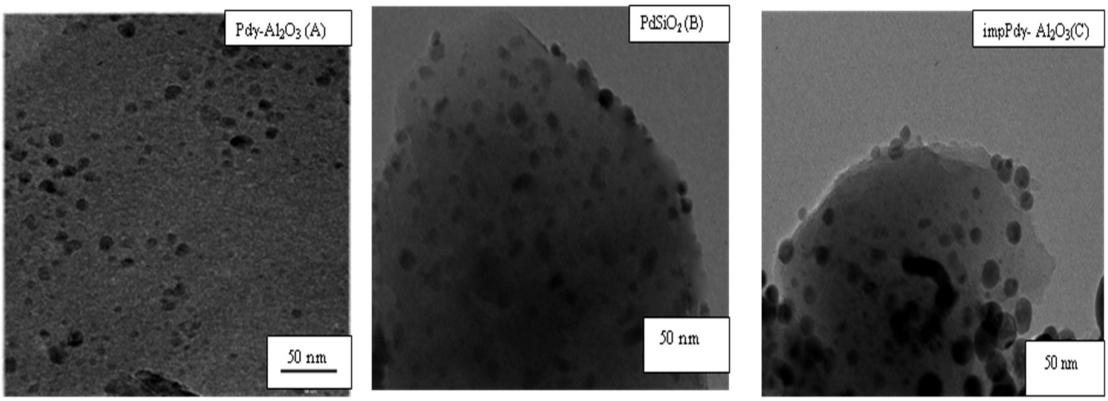

Fig.-2: TEM Images of (A) Pd γ-AAl_2O_3, (B) $PdSiO_2$ and (B) impPdγ-Al2O_3

uniform dispersion with controlled particle size. The TEM micrographs provide the average particle size of PdO as 5.2 nm, 5.6 nm, and 15.2 nm for PdγAl_2O_3 [Fig.-2 (A)], $PdSiO_2$ [Fig.-2 (B)], and impPdγ-Al_2O_3 [Fig.-2 (C)], respectively. This is in good agreement with the XRD results discussed earlier in section [Fig.-1]. TEM image of impPdγ-Al_2O_3 catalysts showed that particle shape is controlled; most of the particles are spherical, but both particle size as well as particle distribution are not controlled. Figure-3 shows the DRUV-VIS spectra of palladium-containing Al_2O_3, γ-Al_2O_3, and SiO_2 supported catalysts. It can be seen from Fig.-3 (b, c, d, e, f) that the sample shows two prominent bands (a broad band at ~ 320 and 360 nm) in the UV region, accounting for the ligand-to-metal charge transfer transitions involving Pd^{2+} species. The same absorption is observed in all Pd-containing catalysts, which indicates that the as-synthesized as well as calcined Pdγ-Al_2O_3 catalysts contain octahedral substituted Pd^{+2} species. The broad absorption band extending into the visible region at 458 nm (d-d transition) due formation of PdO was observed. This is in good agreement with the XRD results discussed earlier in Fig.-1. Significant spectral changes are observed when comparing the spectra of fresh (e) and used (f) Pdγ-Al_2O_3 catalysts. The shifts in absorption intensity and band positions suggest potential structural transformations, Pd nanoparticle aggregation, or oxidation state modifications after catalytic testing.

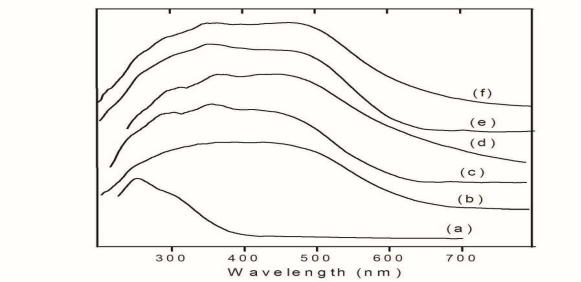

Fig.-3: DRUV-Vis. Spectra of (a) Al_2O_3, (b) Pd-Al_2O_3, (c) $PdSiO_2$, (d) Pdγ-Al2O3, and (e) Pdγ-Al_2O_3 Fresh and (f) Pdγ-Al_2O_3 used Catalysts

These observations highlight the dynamic nature of the Pd species during reaction conditions sharp prominent peak at approximately 646 cm^{-1} in all calcined Pdγ-Al_2O_3, Pd-Al_2O_3, and $PdSiO_2$ catalysts shown in Fig.-4, which is characteristic of metal oxide vibrations. The formation of PdO was clearly observed by Raman spectroscopy. It is very simple to make a quantitative discussion on the correlation of the amount of palladium with the present Raman and high-angle XRD experimental data.

Catalytic Activity Study for the Reduction of NO by CO

Influence of Preparation Methods on the Catalytic Activity of Palladium Supported γ-Al_2O_3 Catalysts

Figure-5 displays the status of NO-CO treated by palladium-supported impPdγ-Al_2O_3 and Pdγ-Al_2O_3 catalysts prepared from two different methods as a function of reactor temperature from 150 to 350 °C.

The NO conversion is a criterion to value the catalyst's activity. The impPdγ-Al_2O_3 catalyst exhibits less catalytic performance in the NO reduction reaction, with NO conversion starting at 175 °C, reaching 100% at 310 °C.

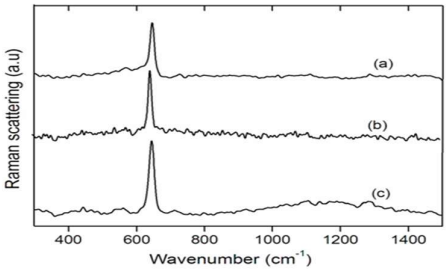

Fig.-4: Raman Spectra of Calcined (a) Pdγ-Al_2O_3, (b) $PdAl_2O_3$ and (c) $PdSiO_2$ Catalysts

CO conversion depicts a similar trend; it initially elevates with reaction temperature and reaches about 36-37% at 320 °C for impPdγ-Al_2O_3, then it remains constant with higher reactor temperature. Consequently, the inferior performance of the impPdγ-Al_2O_3 catalyst, the Pdγ-Al_2O_3 catalyst exhibits activity commencing at 140°C and accomplishing 100% at 235°C, catalysts exhibited excellent catalytic performance. The lowest performance of the impPdγ-Al_2O_3, having similar palladium loading, is mostly attributed to its larger Pd particle size and consequently to its lower palladium surface area. It has already been shown that small palladium particles (Pd particles) work better than bigger Pd particles at reducing NO by CO. In addition, it has been found that the tiniest palladium particles notably achieved N_2 and low N_2O; however, bigger particles generated maximum amounts of N_2O and minimized N_2. The results above show that the preparation methods for the catalyst for NO reduction have a big effect on the amount and size of active PdO species, as well as the activity of the metal on the support. In addition, the HDP method might be useful for making highly active noble metal-supported catalysts because it gets chlorine out well. This study discovered that the amount of exposed palladium determines the activity of the catalysts. This means that the particle size of the palladium particles is inversely related to how much metal clumps together at the pore mouths. So, the HDP method is used for further studies of the effect of support on the activity of catalysts.

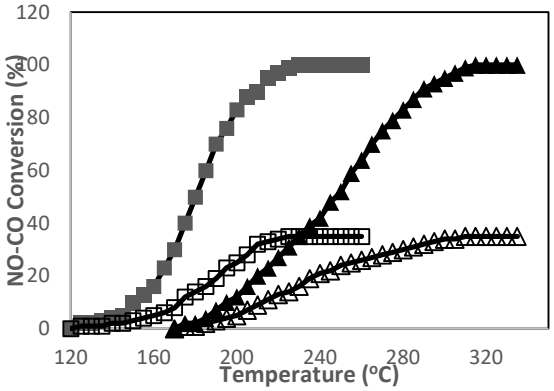

Fig.-5: Effect of Preparation Methods on Palladium Supported γ-Al_2O_3. [NO (-■-), CO (-□-)] Pdγ-Al_2O_3], [NO (-▲-), CO (-Δ-)] impPdγ-Al_2O_3 Catalysts

Influence of Different Supports on Palladium Catalyst Performance Prepared by the HDP Method

This method proved to be effective in producing highly active Pd catalysts. It will be interesting to see how well palladium works as a catalyst on different supports. The oxides used as supports were γ-Al_2O_3, Al_2O_3, and SiO_2. Figure-6 shows a comparison of the catalytic activity of palladium-supported Pdγ-Al_2O_3, $PdAl_2O_3$, and $PdSiO_2$ catalysts for the reduction of NO by CO. We aimed to check whether the γ-Al_2O_3 support was essential for the highly active palladium catalysts. The PdγAl_2O_3 and $PdAl_2O_3$ catalysts were found to have similar catalytic activity, but higher than that of $PdSiO_2$ catalysts. NO conversion (25%) was observed at 175°C for PdγAl_2O_3, and $PdAl_2O_3$ reached 100% at 225°C and

235°C, respectively, whereas NO conversion (25%) was observed at 235 °C. $PdSiO_2$ reached 100% at 265 oC. The amount of NO conversion varied with the different supports, following the order of Pdγ-Al_2O_3> $PdAl_2O_3$> $PdSiO_2$. Different types of interaction between the PdO active species and supports cause a change in activity. These studies Fig.-6 reveal that Pdγ-Al_2O_3 catalysts with an average PdO particle size of 5.2 nm showed high catalytic activity, possibly owing to the low particle size, high and uniform dispersion of Pd active sites on γ-Al_2O_3 support.

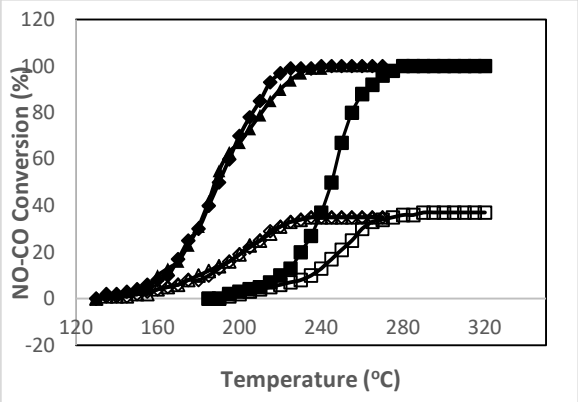

Fig.-6: Effect of Different Supports on the Catalytic Activity of Palladium [NO (-♦-), CO (-◊-)] Pdγ-Al_2O_3, [NO (-▲-), CO (-Δ-)] $PdAl_2O_3$ and [NO (-■-), CO (-□-)] $PdSiO_2$ Catalysts Supported by HDP Method

CONCLUSION

Different techniques successfully characterized all the Catalysts. The type of support adopted and the methodology used for depositing palladium oxide directly affect the catalytic efficacy of the evaluated catalysts. The catalysts produced via the HDP method exhibit higher activity than comparable ones produced from the impregnation method. The particle size of palladium species depends on the method used to deposit it. It is noted that palladium-supported catalysts have been synthesized using the HDP methodology with ~100% loading effectiveness, revealing tiny particle sizes with nanometer-scale dimensions (4–6 nm). This may be due to high dispersion and smaller size of palladium oxide particles formed along the surface of γ-Al_2O_3.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-13: Climate Action*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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