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Gas phase hydrogenation of phenol over supported palladium catalysts

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Abstract

A series of palladium supported on alumina, with Pd variation from 0.5 to 7.0 wt%, was prepared by wet impregnation method and characterised by XRD and CO chemisorption measurements. The catalysts were evaluated for a gas phase hydrogenation of phenol in a fixed-bed reactor at 503 K under normal atmospheric pressure. Palladium content beyond 3 wt% has no significant effect on the turnover number of phenol hydrogenation. The order of the reaction with respect to phenol partial pressure was found to be negative and increased from -0.13 to 0.46 with increasing temperature (473–533 K). The apparent activation energy (E_a) of the process was found to be 30 kJ/mol. On the basis of our results an electronic effect is envisaged for the higher catalytic behaviour of calcium-promoted Pd/Al_2O_3.

Keywords: Adsorption; Dispersion; Metal area; Kinetics; Activation energy

1. Introduction

The gas phase hydrogenation of phenol to cyclohexanone is an important industrial reaction for the production of caprolactum [1]. The single-step vapour phase process over supported palladium catalysts has a commercial advantage, particularly in terms of capital costs and energy savings [2]. Supported Pd catalysts have been studied in a number of hydrogenation reactions of industrial importance to produce value-added products [3]. The activity and product selectivity of the reaction depend to a large extent on dispersion and on the size of the metal crystallites. The correct choice of support is therefore crucial in designing a supported catalyst with the desired activity and selectivity. Magnesia supported catalyst, eventhough shows better catalytic activity, the support MgO is not considered for industrial applications due to its poor mechanical strength. On the contrary, alumina which is more of an industrial choice, suffers from severe deactivation with reaction time. Addition of basic oxide promoters have shown to improve the catalytic behaviour [2]. Studies on the gas phase hydrogenation of phenol are rather limited and no correlation between the dispersion of a metal over the support, metal area, crystallite size and phenol activity has been reported so far. In this communication such a correlation has been attempted for the first time on alumina supported palladium catalysts and also the influence of the modifier on the overall catalytic performance of this reaction has been reported.

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2. Experimental

Supported Pd catalysts containing Pd in different proportions (0.5–7.0 wt%) were prepared by impregnating alumina (Harshaw Al-111-61E; surface area= 234 m^2/g; pore-volume=0.65 cm^3/g) with known concentrations of acidified solutions of $PdCl_2{\cdot}xH_2O$. The calcium-modified palladium catalysts were prepared by impregnating the aqueous calcium nitrate solutions of appropriate concentrations of calcium on alumina before the addition of palladium. The catalysts were dried overnight and calcined at 723 K for 5 h.

X-ray diffraction (XRD) patterns of the catalysts were taken using the Philips PW 1140 diffractometer with Ni filtered Cu K$_\alpha$ radiation (λ=1.54 Å).

Carbon monoxide adsorption measurements were carried out at room temperature in a conventional constant volume adsorption system on the catalyst reduced at 723 K for 3 h in a hydrogen flow (0.26 mol/h). A stoichiometry Pd/CO=1 and a Pd surface density of 1.27×10^{19} atoms/m^2 were assumed [4].

Gas phase catalytic hydrogenation of phenol was carried out in a vertical flow type reactor at 503 K under normal atmospheric pressure. A mixture of phenol plus cyclohexane (1:2 w/w ratio) was fed over a pre-reduced catalyst (ca. 0.5 g) at a fixed rate by means of a motorised syringe. The liquid products were analysed by GC using a column packed with Carbowax 20 M on Chromosorb W.

3. Results and discussion

The detailed procedure adopted for the determination of dispersion, metal area and crystallite size from the irreversible CO uptake has been reported elsewhere [5]. A correlation between some of these catalyst properties and palladium loading is shown in Fig. 1. Both dispersion and metal area decrease with metal loading. Metal area shows a sharp decrease with palladium content up to 3 wt% and there after remaining nearly the same. The crystallite size, however, shows an opposite trend. It increases with metal loading and remains steady above 3 wt% of palladium. A constant dispersion with relatively uniform crystallite size with increasing loading indicates the absence of any large agglomeration of metallic palladium. This is in agreement with the XRD results, wherein the absence of large metal crystallites on both calcined and reduced samples of Pd/Al_2O_3 were observed. The decrease in metal area with increasing palladium loading may however, be attributed to the nonavailability of a number of metal crystallites for CO adsorption which is a measure of metal area.

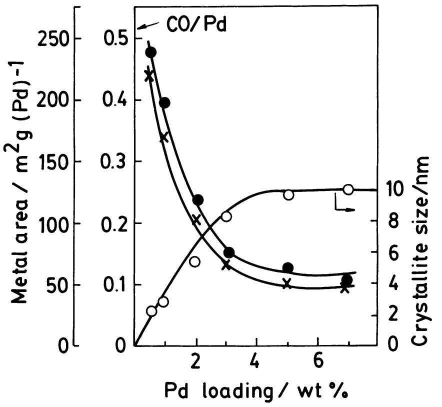


Fig. 1. Effect of metal loading on dispersion (●); crystallite size (○); and metal area (×).

An interesting correlation between the phenol hydrogenation activity, as expressed by turnover number (TON) (i.e. molecules of phenol converted per atom of palladium on the surface), with metal area and dispersion is shown in Fig. 2. The TON increases with metal area irrespective of metal loading. It can also be

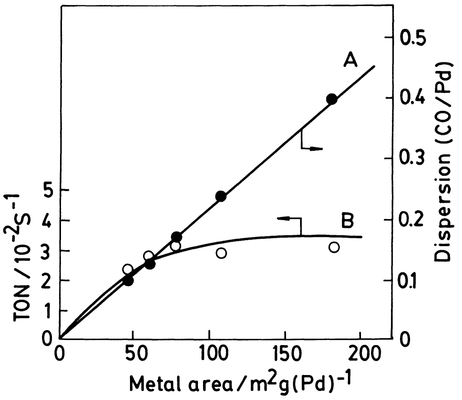


Fig. 2. A correlation between metal area, dispersion (●) and turnover number, TON (○) for phenol hydrogenation over Pd/Al_2O_3 catalysts at 503 K. H/Phenol=5.4, and WHSV=0.027 mol/h g cat.

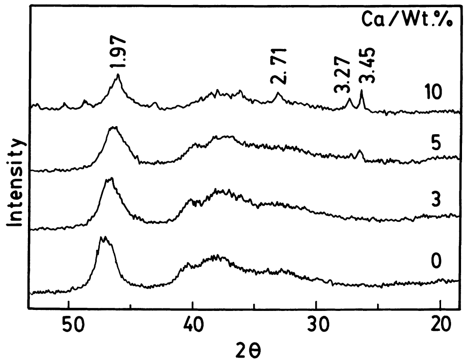


Fig. 3. XRD spectra of alumina and Ca-promoted alumina calcined at 723 K for 5 h.

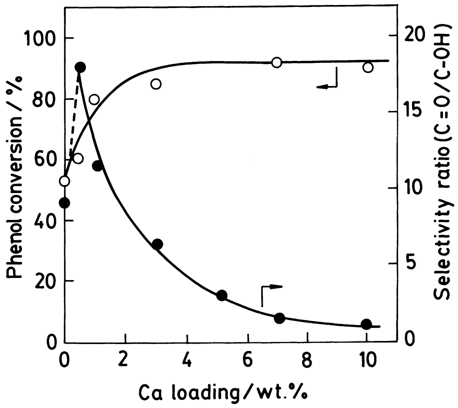


Fig. 4. Effect of calcium on phenol conversion (○) and selectivity ratio (●); C=O, cyclohexanone and C–OH, cyclohexanol; T=503 K, H/Phenol=5.4, WHSV=0.027 mol h g cat.

seen that the dispersion of palladium increases with metal area. The comparison of the two plots (Fig. 2(A) and (B)) leads to a correlation of smooth variation of phenol hydrogenation activity and dispersion with metal area. From Figs. 1 and 2, one could infer that an increase in palladium content, especially above 3 wt% does not necessarily increase the metal area available for CO adsorption or hydrogenation of phenol, eventhough crystallite size and dispersion do not vary much.

The gas phase hydrogenation of phenol over Pd/Al_2O_3 catalyst together with CO adsorption experiments reveal that TON for phenol conversion decreases with metal loading beyond 3 wt% of palladium and increases with metal area per gram of metal indicating that all the possible palladium atoms are not available for CO adsorption or hydrogenation activity. Increase in palladium loading beyond 3 wt% has no significant effect on the TON of phenol hydrogenation.

X-ray diffraction (XRD) patterns (Fig. 3) of calcined aluminas with different calcium contents are compared together with an alumina support calcined at the same temperature. No significant differences in spectrum is noticed between calcium-modified aluminas (<5 wt%) and unmodified alumina samples. This indicates that the promoter is well dispersed over alumina. However, when the amount of modifier was increased to 5 wt% and above, the diffraction peak of CaO crystallites (d=3.27 and 3.40 Å) appeared and the intensity of which increased with the modifier content. This is in agreement with the MgO/Al_2O_3 system and a strong interaction between MgO and the support Al_2O_3 has been proposed [6]. The peak at d=2.71 Å, a trace quantity at a calcium loading of 10 wt% and above corresponds to a type of calcium–alumina compound, viz $Ca_{12}Al_{14}O_{33}$. In addition, the intensity of the peak at d=1.97 Å, a characteristic peak of alumina, has reduced considerably with increased amount of promoter.

The influence of modified Pd (1 wt%)/Al_2O_3 catalyst on phenol conversion and product selectivity is shown in Fig. 4. The conversion of phenol increases with increasing calcium content and beyond 3 wt% of calcium, the change in conversion is not significant. It appears that the product selectivity between cyclohexanone and cyclohexanol depends much on the amount of modifier being added to alumina. The selectivity for cyclohexanone increases with decreasing amount of calcium over alumina. The addition of alkali metal atoms is known to decrease the acidity of the support surface [7]. The higher selectivity of cyclohexanone at lower concentration of calcium modifier suggests that on a lesser acidic support, the adsorption of phenol in the form of phenolate with its ring nonplanar mode to the surface [8,9] would promote more of acid catalysed isomerisation of cyclohexanone to cyclohexanone formation. However, at higher concentration of calcium modifier, the selectivity of cyclohexanone falls since the neutralisation of more acidic sites inhibits the acid catalysed isomerisation. It is likely that the increase in phenol activity may be attributed to a strong interaction between the promoting ion and the

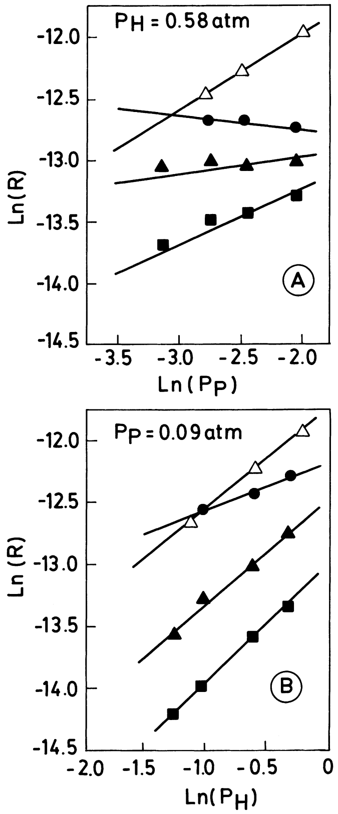


Fig. 5. Effect of partial pressure of phenol (A) and hydrogen (B) on the reaction rate over Pd/Al_2O_3 catalyst at different temperatures (T (K)=(●) 473; (▲) 503; (■) 533} and Pd/Ca 1 wt%-Al_2O_3 catalyst at T=(△) 503 K. H/Phenol=5.4 and WHSV=0.027 mol/h g cat.

oxygen atom of the phenolate thereby enhancing the rate of desorption of the product which is the rate determining step in the hydrogenation of phenol [10].

To explain the complex situation that arises between the adsorbed phenol and hydrogen on the surface of the catalysts, only a few papers have been reported concerning the reaction mechanism and kinetic models [11,12]. Fig. 5 (A and B) shows the influence of partial pressure of phenol (P_P) and hydrogen (P_H) on the rate of phenol hydrogenation (R). A smooth correlation is seen over a wide range of partial pressure (0.05–0.80 atm.) for all three temperatures. This implies a direct dependency between the rate and the partial pressure of the reactants exist and the rate expression can be written in the form of a simple power rate law as

$$R = k(P_P)^x(P_H)^y,$$

where R is the rate of reaction expressed in mol/s g cat and x and y are the reaction orders with respect to phenol and hydrogen, respectively. At 473 K, the order of the reaction is negative with respect to phenol and positive with respect to hydrogen. The variation in x and y with temperature is shown in Table 1. The increase in order of phenol with rise in temperature suggests a weak mode of adsorption on the surface at higher temperatures. This is in agreement with the results wherein the temperature of desorption of phenol was shown to be higher on Pd/MgO as compared to the acidic support [13]. In the case of calcium-modified catalyst, the higher order of the reaction with respect to phenol suggests a large reduction in surface acidity on addition of calcium promoter. The change in acidity, as measured from ammonia chemisorption, was found to be from 52 to 30 μmol/g cat. However, with hydrogen no significant change in the reaction order is noticed (Table 1). From the values of x and y at different temperatures, (Table 1) the average rate constants determined ([14], Appendix A). From the value of average rate constants at various temperatures, apparent activation energy (E_a) was found to be 30 kJ/mol. This is far less as compared to Pd/MgO catalyst where E_a was found to be 63 kJ/mol [14]. This indicates that phenol hydrogenation is a less activated process in Pd/Al_2O_3 as compared to Pd/MgO system.

Table 1
Kinetic data on phenol hydrogenation

Catalyst	Temperature (K)	Reaction order	
		Phenol (x)	Hydrogen (y)
Pd/Al_2O_3	473	−0.13	0.39
	503	0.13	0.87
	533	0.46	0.98
Pd/Ca–Al_2O_3	503	0.65	0.84

The stability of the catalyst with reaction time over modified and unmodified palladium catalysts is shown in Fig. 6. The unpromoted catalyst shows a faster deactivation with time. In a time interval of 8 h, the conversion has decreased from 65% to 40% while the calcium-promoted shows a larger resistance towards deactivation as seen from the marginal fall in phenol conversion from 80% to 76%, which improves further

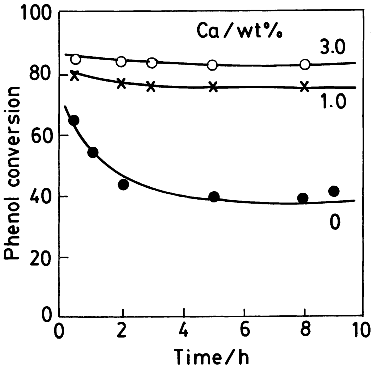
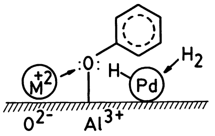


Fig. 6. Effect of time on stream over calcium-promoted and unpromoted Pd/Al_2O_3 catalysts: T=503 K; H/Phenol=5.4; and WHSV=0.027 mol/h g cat.



Scheme 1.

with increasing addition of calcium modifier. The faster deactivation of unpromoted alumina is attributed to the coke formation on the acidic sites of alumina support [15].

The enhancement in phenol hydrogenation activity of calcium-modified Pd/Al_2O_3 catalyst may be due to the enrichment of smaller promoting ions on the surface. The promotional aspects of alkali-doped metal oxide is known to improve the catalytic performance [7]. Based on our results, a reaction mechanism is proposed wherein the positively charged promoting ion interacts with the oxygen atom of the phenolate to weaken the bond strength between the adsorbed phenol and the support surface, thereby enhancing the rate of desorption of the product (Scheme 1).

4. Conclusion

From the adsorption measurements, one could infer that phenol hydrogenation depends on the metal dispersion and metal area. Palladium content beyond 3 wt% has no significant effect on the turnover number of phenol hydrogenation. Addition of calcium modifier at a lower concentration, enhances the selectivity for cyclohexanone. Increase in phenol activity of calcium-modified catalyst may result due to the strong interaction between the promoter ion and the adsorbed phenol on the support surface.

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References

[1] F. Van Peppen, W.B. Fischer, C.H. Chan, Catalysis of Organic Reactions, Marcel Dekker, New York, 1980, p. 141.
[2] I. Dodgson, K. Griffin, G. Barberis, F. Pignataro, G. Tauszik, Chem. Ind. (1989) 830.
[3] P.N. Rylander, Catalytic Hydrogenation in Organic Synthesis, Academic Press, New York, 1974, p. 194.
[4] J.R. Anderson, Structure of Metallic Catalysts, Academic Press, London, 1975, p. 296.
[5] N. Mahata, V. Vishwanathan, Adsorption Sci. Tech. 15 (1997) 165.
[6] C. Qi, T. Bai, L. An, React Kinet. Catal. Lett. 54 (1995) 131.
[7] J.M. Lunsford, Stud. Surf. Sci. Catal. 61 (1991) 3.
[8] R. Taylor, K.H. Lundlum, J. Phys. Chem. 76 (1972) 2882.
[9] K. Tanabe, T. Nishisazaki, in: G.C. Bond, P.B. Wells, F.C. Tompkins (Eds.), Proceedings of the Sixth International Congress on Catalysis, Chemical Society, Letchworth, 1977, pp. 863.
[10] J.R. Gonzalez-Velasco, J.I. Gutierrez-Oritz, J.A. Gonzalez-Marcos, A. Romero, React. Kinet Catal. Lett. 32 (1986) 505.
[11] M.A. Gutierrez-Ortiz, A. Casatano, M.P. Gonzalez-Marcos, J.I. Gutierrez-Ortiz, J.R. Gonzalez-Velasco, Ind. Eng. Chem. Res. 33 (1994) 2571.
[12] V. Hancil, P. Mitschka, L. Berancek, J. Catal. 13 (1969) 435.
[13] G. Neri, A.M. Visco, A. Donato, C. Milone, M. Malentacchi, G. Gubitosa, Appl. Catal. A 110 (1994) 49.
[14] N. Mahata, V. Vishwanathan, J. Mol. Catal. A 120 (1997) 267.
[15] S. Galvango, A. Donato, G. Neri, R. Pietropaolo, J. Chem. Technol. Biotechnol. 51 (1991) 145.