Original Article

Influence of Metal Promoters on Phenol Hydrogenation Activity Over Alumina-Supported Palladium Catalysts

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*Abstract - Series of alkali and alkaline earth promi=oted palladium-alumina (Pd/Al2O3) catalysts were synthesised by incipient wetness method using palladium acetate dissolved in acetonitrile as a precursor for palladium. The palladium dispersion on the catalyst surface was calculated from the chemisorption of the CO molecule. The synthesised catalysts were tested under the vapour phase for the hydrogenation of phenol to cyclohexanone in a down-flow reactor at atmospheric pressure. Among the samples tested, the alkali metal-promoted catalysts showed better phenol activity. A direct correlation ship was observed between the hydrogenation activity and the functionalities of the promoters were observed.*

Keywords – Catalyst, Promoters, Hydrogenation, Reactor, Deactivation .

1. Introduction

Catalytic vapour phase hydrogenation of phenol is industrially important since it is the product cyclohexanone, which is an important intermediate raw material to produce caprolactam. Cyclohexanone is produced by two reaction routes, either by the oxidation of cyclohexane or by the catalytic hydrogenation of phenol [Scheme 1]. Conventionally, the oxidation route is preferred since it is economical and cost-effective. However, the reaction is carried out under severe conditions like high temperature and pressure.
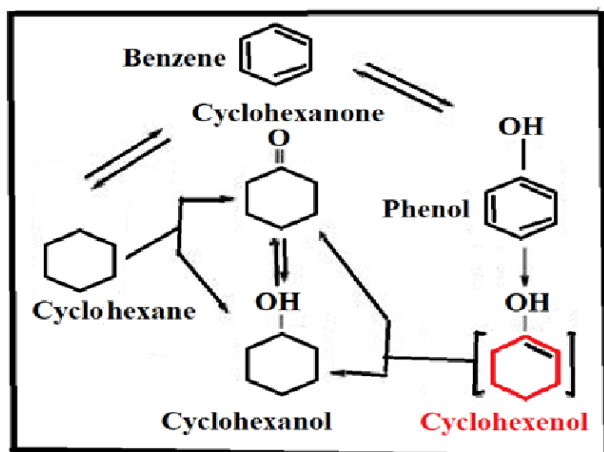
Scheme 1. Different pathways to produce cyclohexane

In addition, it generates a significant quantity of undesirable products, which lower the selectivity of cyclohexanone or the product yield [1]. The catalytic route of hydrogenating phenol can either be a single-step process or two-step. The "two-step" process involves hydrogenation of phenol to cyclohexanol over a Ni catalyst as a first step and then dehydrogenation of cyclohexanol to cyclohexanone on a Cu/Zn catalyst as a second step [2, 3]. The intermediate product, cyclohexanol, formed a stable compound in the two-step process. Also, the dehydrogenation of cyclohexanol to cyclohexanone is highly endothermic and operates at a very high temperature [4]. However, in the case of a single-step process, there is a direct conversion of phenol to cyclohexanone through the formation of an intermediate called cyclohexenol which is highly unstable. The intermediate cyclohexenol, being unstable, readily isomerises to cyclohexanone. This direct step of conversion saves the absence of the endothermic dehydrogenation step. The single-step process is advantageous in terms of energy savings since it avoids the dehydrogenation of cyclohexanol to cyclohexanone. The estimation of cyclohexanol purification and endothermic dehydrogenation step would yield an energy saving of 500 kcal/kg production of cyclohexanone.

Supported metal catalysts are commonly used for hydrogenation reactions. Supports ensure better dispersion and stability for the active metals to hydrogenate the reactant molecule. The catalytic vapour phase hydrogenation of phenol has been studied on different types of supported metal catalysts [5]. The deposition of noble metals on acid-based supports was used in several hydrogenation reactions to give valuable industrial products. Supported palladium on alumina (Pd/Al2O3) or magnesia (Pd/MgO) are commonly used for phenol hydrogenation. Magnesia-supported metal catalysts, though showing better catalytic performance in terms of phenol conversion and cyclohexanone selectivity, are often not considered due to the poor mechanical strength of MgO [6]. Pd/Al_2O_3 catalysts are commonly used for the title reaction. The support material, Al_2O_3 being acidic, undergoes faster deactivation during the reaction. It is known that adding basic metal oxides as promoters or modifiers to alumina improves the phenol hydrogenation activity of the reaction. Studies on supported palladium-alumina catalysts with the addition of basic metal oxides as promoters for the title reaction are limited. The present

communication shows the influence of alkali and alkaline metal oxides as promoters on the Pd/Al$_2$O$_3$ catalyst studied for the title reaction.

2. Materials and Methods

Commercial alumina (Al$_2$O$_3$) from the Harshaw company was used as a support material. It was modified by a developing method by adding nitrate solutions of alkali and alkaline metals. The synthesised samples were calcined at 723 K for 5 h. This was followed by adding a clear solution of palladium acetate (metal content = 1 wt%) using acetonitrile over was deposited over each as synthesised samples of modified alumina. The final catalysts were again dried and calcined as did earlier.

CO chemisorption was studied at 298 K. The effective dispersion of palladium on the surface of the catalysts was determined at a constant volume on the reduced catalyst in a hydrogen flow at 573 K for 3 h. Pd/CO = 1 as a stoichiometric ratio, and the surface density of Pd = 1.27×10^{19} atoms m^{-2} was used for calculation.

Gas-phase phenol hydrogenation was studied in a tubular reactor at 503 K under normal pressure. Phenol feed was made easier by adding cyclohexane. Under the reaction conditions, no dehydrogenation or decomposition of cyclohexane was noticed. The mixture of phenol and cyclohexane in the ratio 1:2 wt/wt was introduced over a catalyst (ca. 0.5 g) which was reduced earlier in hydrogen using a syringe. After an interval of every 1 hour, the reaction products were analysed by a GC using a column of Carbowax 20 M. The reaction rates were studied under differential mode. Under the given reaction conditions, cyclohexanone was the major product with 95% and above. No dehydration products were observed in the analyte.

3. Results and Discussion

Our earlier study on X-ray examination of the metal-promoted Pd/Al$_2$O$_3$ catalysts has shown the absence of PdO crystallites on the surface [7]. This suggests that smaller crystallites of PdO are highly dispersed on the alumina surface, which is not large enough for X-ray detection.

The results of CO chemisorption measurements of several basic metal oxides promoted Pd/Al$_2$O$_3$ catalysts are shown in Table 1. The unpromoted (Pd/Al$_2$O$_3$) catalyst shows palladium dispersion higher than promoted (Pd/M-Al$_2$O$_3$) catalysts. Among the alkali-promoted catalysts, the smaller promoter ion (Li$^+$= 0.68 A^0) has a lesser influence on metal dispersion than the larger size ion (Cs$^+$ = 1.67 A^0). Among the promoters, the alkali metal ions showed higher phenol activity than the alkaline earth metal ions. This effect has been attributed to a more favorable activation of hydrogen by the electronically modified metal sites. It is known that the dispersion of smaller palladium crystallites at a higher level has an electron density that is much lower **[8]**. This implies that smaller palladium particles on the promoted (Pd/M-Al2O3) catalysts show more hydrogenation activity per site than the unpromoted catalyst. This suggests that the net charge density at the metal site in the promoted catalyst is responsible for the higher phenol activity [9].

Table 1. Effect of promoters on Palladium-alumina catalysts

	Pd / Al$_2$O$_3$	Pd / M$^@$-Al$_2$O$_3$						
Metal Group		**Alkali Metals**				**Alkaline Earth Metals**		
Promoter (M) (1 wt%)	None	Li	Na	K	Cs	Ca	Sr	Ba
Pd dispersion (%)	48	33	30	39	43	62	48	51
Phenol activity mol. s^{-1}g^{-1}.cat	4.0	6.6	6.6	5.5	5.1	5.9	5.6	5.2

@ where M stands for the alkali and alkaline-earth metal promoters

The influence of the relative charge transfer capacity (CTC) of the promoter oxides on phenol hydrogenation activity is shown in Figure 1. Phenol hydrogenation activity is dependent on CTC, and the activity was enhanced with increasing CTC. The promoted Pd/Al$_2$O$_3$ catalysts showed higher reaction rates. The observed dependence on CTC suggests that the net Charge density at Pd sites is critical in determining hydrogenation activity. It is reported that base metal oxides doping markedly affect hydrogenation characteristics by enriching the metal particles' electrons [6, 10]. It is well known that the d-character of Pd influences the hydrogenation activity. A modification of the electron density of Pd can alter the degree of substrate/surface interaction, which can considerably impact catalysis [11]. Smaller ions have a larger associated CTC. *I*n the case of the alkali and alkaline promoters, the smaller ions in both series, *i.e.,* Na$^+$ and Mg^{2+}, exhibited the greatest level of promotion.
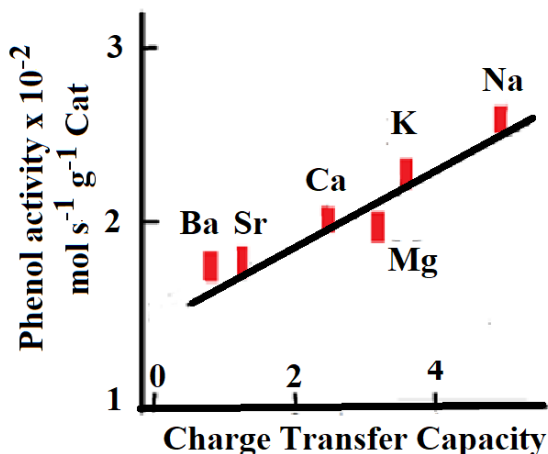
Fig. 1 Effect of charge transfer capacity on promoted Pd/Al₂O₃ catalysts

In supported catalysts, usually, one expects a correlation between the dispersion of metal and the reaction rate. But such a relationship seems to be absent in the present investigation. This implies some periodic functionalities of the promoter ions may be responsible for the increase in phenol activity. Such a type of relationship is shown in the case of Pd/M-Al₂O₃ catalysts (**Figure 2**).
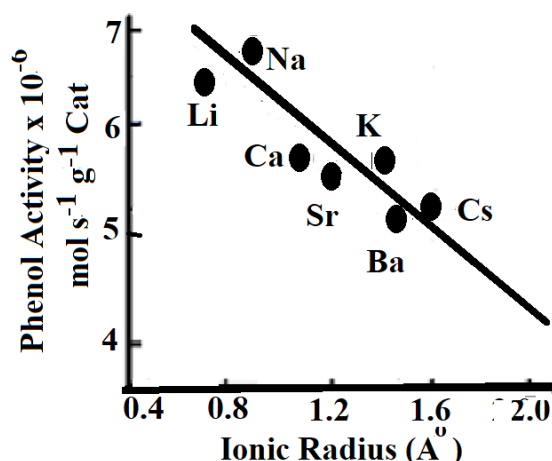

Fig. 2 Effect of ionic radius of metal promoters on phenol activity over Pd/Al₂O₃ catalysts.

The direct correlation attributes to the interrelationship between the phenol activity and the promoting alkali/alkaline earth metal ions.

The decline in hydrogenation activity with time on stream has been attributed to the deactivation of the catalyst. The stability of the catalyst with time-on-stream (TOS) for the two types of catalysts is shown in **Figure 3**. The base metal promoted catalysts show better resistance towards deactivation than the unpromoted catalyst. During the 6h of the reaction,
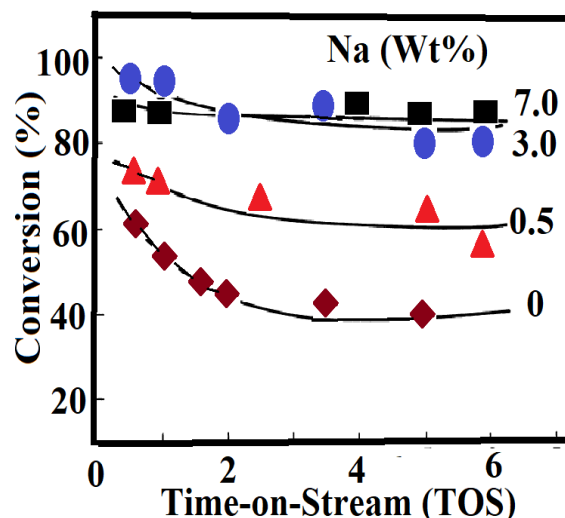

Fig. 3 The effect of reaction time on the conversion of phenol over Na promoted Pd/Al₂O₃ catalysts. Reaction conditions: T= 503K, H/Phenol ratio =5.4.

The conversion has declined to 40% from 65%. Among the promoted catalysts, b the sodium promoted Pd/Al₂O₃ catalyst shows higher stability towards coke formation, which improves with more sodium content. The faster deactivation of the unpromoted catalyst is attributed to the formation of coke deposits on the acidic sites of Al₂O₃ support material [12].

The increase in phenol activity on promoted catalysts may be due to the presence of smaller promoter ions on the catalyst surface. This behaviour of base metal oxide doped to improve the catalytic performance is reported in the literature [4, 13]. Based on our findings, a schematic mechanism is proposed (Scheme 2). According to this mechanism, the positively charged promoter ion reacts with the phenolate to reduce the bond strength between the phenol, which is strongly adsorbed, and the catalyst surface, thereby promoting the product's desorption rate cyclohexanone (Scheme 2).
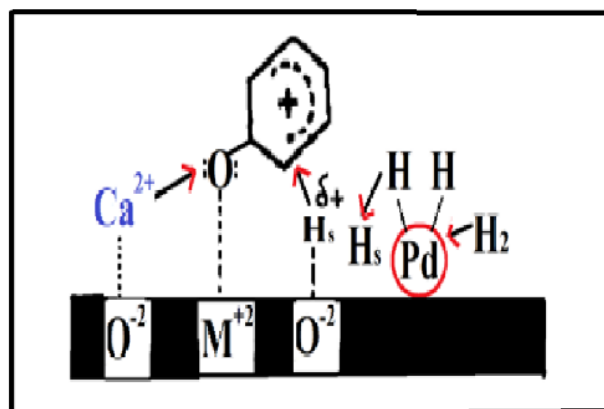
Scheme 2. The influence of promoter ion on Pd/Al₂O₃ catalysts.

4. Conclusion

Alkali metal cations promoted Pd/Al$_2$O$_3$ catalysts show higher phenol hydrogenation activity, while the alkaline earth promoted cations exhibit better thermal resistivity towards coke formation. The enhanced phenol activity in the case of promoted Pd/Al$_2$O$_3$ catalysts suggests the presence of a strong interaction between the promoter cation and the phenol molecule adsorbed strongly on the catalyst surface. It is also believed that the alkali-promoted cations may modify the net charge density at the reactive site to a significant extent. It is very evident from the results that the Pd/Na-Al$_2$O$_3$ catalyst will be ideal for the gas phase hydrogenation of phenol through a single-step process. All these factors suggest the promotional aspect of the promoted Pd/Al$_2$O$_3$ catalysts.

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