**Predictive modelling on aerobic oxidation of benzyl alcohol by ceria-based catalysts based on past research publications**

**Introduction.**

Aerobic oxidation of benzyl alcohol is an important reaction from both academic and industrial point of views. Academically, benzyl alcohol gathers attention due to its high affinity towards oxidation and generation of non-enolizable aldehydes as products. It is often used as a probe reaction to evaluate the ability of catalysts toward oxidation of alcohols1,2. Industrially, its major oxidative product, benzaldehyde, is known as a versatile chemical ingredient in agrochemical, pharmaceutical, perfumery and many other fine chemical industries 3,4. Therefore, in recent years, a tremendous amount of works has been done to improvise the benzyl alcohol oxidation in terms of ambient reaction conditions, efficient catalyst designing and achievement of desired yield.

However, reaction optimization is rather complicated procedure that depends on many different factors like nature of catalysts, solvents, reaction temperature, pressure, time duration etc. Moreover, the nature of catalysts is subject to further diverse factors like type of supports, particle size, use of promoters, surface area, morphology etc. As for example, the aerobic oxidation of benzyl alcohol have been studied with different supports like TiO2 5–8 CeO2 1,2,8–14, MnO24,15–17, active noble metals like Au1,2,9,10,13, Pd1,8,11,14, different metal promoters like Bi2,9, Mn10, Sn18, Zr19 , different solvents like toluene9, cyclohexane19, water20 or without any solvent1,14 and at different pressure ranges like 0.1 MPa 9, 0.2 MPa 19 and 0.3 MPa1 .

In the presence of such wide range of variables, slight change in even one of those factors can highly influence the research results, in certain cases showing very different outcomes21. However, it is rather arduous to optimize all those parameters in a single experimental study. Therefore, most studies focus on some factors in a reaction, keeping the other factors constant. However, as the determining factors are interlinked, change in one factor might influence the other, therefore many fundamental aspects are overlooked.21 Even so, the wide range of experimental works done in the past can be used to generate predictive models to generate expectable outcomes of an unstudied condition.

In this work, statistical and data analysis models have been used to predict the outcome of different catalytic results of aerobic oxidation of benzyl alcohol using CeO2based catalysts.

**2. Materials and Methods.**

**2.1. Data Extraction.**

4 research publications1,9,11,19 on aerobic benzyl alcohol oxidation with CeO2based catalysts are taken and 70 datapoints are extracted. The different variables and factors in the datapoints are mentioned in Table 1

**Table 1. Different Predictor Variables, Their Types, Ranges and Values**

|  |  |  |  |
| --- | --- | --- | --- |
| **Variables** | **Variable Type** | **Range/Values** | **Output** |
| Noble Metal | Categorical | Au, Pd | 1. **Conversion of Benzyl Alcohol** 2. **Yield of Benzaldehyde** |
| Weight% of Noble Metals | Continuous | 0-2.5 % |
| Particle Size of Noble Metals | Continuous | 0-6.4 nm |
| Preparation Procedure of Noble Metals | Categorical | Deposition-Precipitation(DP),  Wetness Impregnation (WI),  Incipient Wetness Impregnation (IWI) |
| Calcination Temperature of Noble Metal Nanoparticles | Continuous | 298K – 973K |
| Support (CeO2) Morphology | Categorical | Nanorods, nanocubes, nanopolyhedra, nanoparticles, mesoporous |
| Metal Promoters | Categorical | Bi, Zr |
| Mole Fraction of Metal Promoters | Continuous | 0-0.4 |
| Solvents | Categorical | Toluene, Cyclohexane, n-Heptane, Flurotoluene, 1,4-Dioxane, Methanol, Water, No-solvent |
| Molar Concentration of Benzyl Alcohol | Continuous | 1-9.62 M |
| Reaction Temperature | Continuous | 353-393K |
| Reaction Pressure | Continuous | 0.1-0.3 MPa |
| Reaction Time | Continuous | 0.25-6 hour |

* 1. **Computational Details.**

The statistical predictions were done using Classification Learner and Regression Learner applications in Matlab R2019a platform. K-fold cross validation was applied on the data, i.e. the data was divided into “k” number of subsets (here k =5), and the statistical models were applied on 4/5th of the data to generate a trained model. The trained model was then applied on the remaining 1/5th of the data to validate the predictions. The process was repeated k times (i.e. 5 times) to validate each subset. Initially all the classification and regression models were applied (including Regression Tree, Support Vector Machines, Linear Regression etc) to get the most accurate prediction of the morphology of support and the catalytic conversion. The values with high predication accuracy are reported.

1. **Results and Discussions.**
   1. **Prediction of Catalytic Conversion of Benzyl Alcohol**

Different regression models were used to predict the percentage conversion of benzyl alcohol to benzaldehyde using the predctors/input variables described in **Table 1.** The **RMSE** (Root Mean Square Error) values show the closeness of actual datapoints to the predicted values. A low RMSE value shows more accurate prediction. The **R2** values are used to estimate the good fit of the results in a particular model. The equations followed to determine the RMSE and R2 values are given below:

**……………….**Eq(1)

**………………**Eq (2)

Where pi and ti are predicted and actual values of percentage conversion of Benzyl Alcohol respectively, is the mean of ti values and n is the number of experiments.

The optimization of the Artificial Neural Networ model had shown R value of 0.96 and RMSE value of 7.72

* + 1. **Estimation of the Relative Importance of Different Variables**

**Table 2.**

|  |  |  |  |
| --- | --- | --- | --- |
| **Variable** | RMSE without Variable | Difference in RMSE |  |
| Noble Metals | 33.95 | 26.23 |  |
| Metal Promoters | 17.42 | 9.7 |  |
| Type of CeO2 | 30.00 | 22.28 |  |
| Solvents | 32.36 | 24.64 |  |
| Volume of Solution | 19.08 | 11.37 |  |
| Concentration of Benzyl Alcohol | 13.56 | 5.85 |  |
| Reaction Time | 37.76 | 30.04 |  |
| Reaction Temperature | 167.7 | 160 |  |
| Catalyst Amount | 17.67 | 9.95 |  |

The relative importance of the catalyst properties and the operational variable is shown in Table 2. Reaction Temperature can be observed as the single most important factor, due to its long range of effect and fundamental importance in reaction kinetics21. The reaction time also had shown high significance, however, its effect was observed to be substantially less than the reaction temperature, probably because effective reaction time is dependent on many other factors like the nature of the catalysts or other operational variables, which share the predictability of the outcome in a manner similar to the reaction time.

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