

# FLUIDIZED BED REACTOR FOR THE INTENSIFICATION OF GAS PHASE PHOTOCATALYTIC OXIDATIVE DEHYDROGENATION OF CYCLOHEXANE

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## Summary

The behavior of a two-dimensional laboratory scale fluidized-bed catalytic reactor for the photocatalytic oxidative dehydrogenation of cyclohexane to benzene has been studied employing a molybdenum based catalyst and a titania-alumina mixed oxide as support. A preliminary mathematical model is proposed for the evaluation of the effect of the main factors affecting the overall reactor performances. Experimental data evinced that the reaction rate is not depending by the oxygen concentration, whereas it depends on cyclohexane concentration according to Langmuir-Hinshelwood kinetic. Taking into account that the interaction between photoexcited molybdate and adsorbed cyclohexane is the rate limiting step, the functionality in light intensity was found. The mathematical model well describes the performances of the photocatalytic fluidized bed reactor for all operating conditions examined.

## Keywords

Photocatalysis, fluidized bed reactor, kinetic parameters, mathematical modeling.

## Introduction

In our previous work, we reported that employing  $\text{MoO}_x/\text{TiO}_2$  catalysts under UV illumination centred at 365nm, cyclohexane may be selectively oxidised to benzene in the presence of gaseous oxygen at temperature of 35°C in a gas-solid fixed bed reactor (1). More recently we also showed that it is possible to realize the same reaction on  $\text{MoO}_x/\text{TiO}_2$  catalysts by using a photocatalytic fluidized bed reactor (2). In order to obtain good fluidization, physical mixtures with  $\alpha\text{-Al}_2\text{O}_3$  at different percentage of Mo-titania catalysts were experimented. An alternative is to realize  $\text{TiO}_2\text{-Al}_2\text{O}_3$  mixed oxide catalytic supports.  $\text{MoO}_x/\text{TiO}_2\text{-Al}_2\text{O}_3$  catalysts showed an improved synthesis of benzene with respect to  $\text{MoO}_x/\text{TiO}_2\text{-alumina}$  physical mixtures (3). In the present work, the parameters influencing the kinetic of photocatalytic oxidative dehydrogenation of cyclohexane to benzene has been studied in a laboratory scale gas-solid fluidized bed photoreactor on Molybdenum based catalyst by using a titania-alumina mixed oxide as support. The effects of light intensity and of hydrocarbon and oxygen concentration were experimentally analyzed and a preliminary mathematical model was developed.

## Experimental

Titania-alumina support was prepared following the procedure reported in (3). An aqueous solution of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  was used as  $\text{MoO}_3$  precursor to

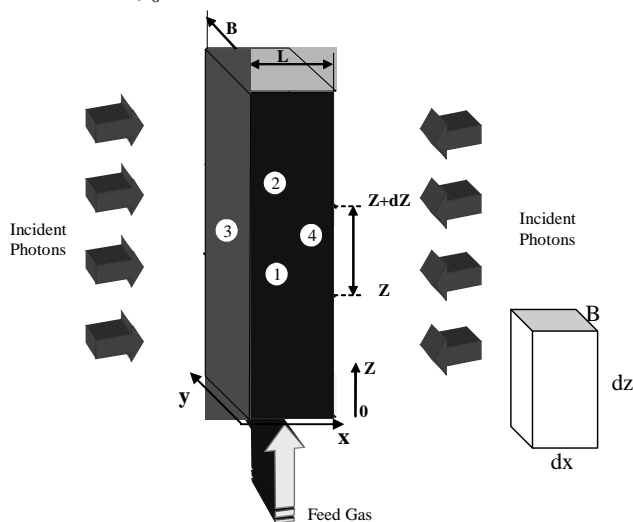
impregnate the alumina-titania support. The calcined catalyst (10MoPC100Al) contained 10 wt % of  $\text{MoO}_3$  as nominal loading. A total gas flow rate of 50 l/h(STP) was introduced into the two dimensional photocatalytic fluidized bed reactor. The reactor was illuminated by two UV-LEDs modules positioned in front of the pyrex windows. Each UV-LEDs module consisted of 40 pieces (supplied by Nichia Corporation) with a very narrow wavelength distribution, centred at 365 nm. The reaction temperature (120 °C) was controlled by a PID controller connected to a heater system and installed into the reactor. Catalytic tests were carried out feeding  $\text{N}_2$  stream containing a cyclohexane concentration ranging between 500 and 6000 ppm, with  $\text{O}_2/\text{cyclohexane}$  and  $\text{H}_2\text{O}/\text{cyclohexane}$  ratio respectively of 1.5 and 1.6. Photocatalytic tests were also performed at various  $\text{O}_2$  partial pressures with an initial cyclohexane concentration equal to 1000 ppm. Catalyst weight was 14 or 20g. The gas composition was continuously measured by an on-line quadrupole mass detector (Trace MS, ThermoQuest) and a continuous  $\text{CO-CO}_2$  NDIR analyser (Uras 10, ABB).

## Results

The analysis of products distribution at the reactor outlet during UV irradiation of 10MoPCAl catalyst disclosed only the presence of benzene and traces of cyclohexene,

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and no deactivation tendency is observed. The comparison of photocatalytic performances in the steady state of 10MoPC100 as a function of the initial cyclohexane and oxygen concentration evidenced that the behavior can be well described by the Langmuir-Hinshelwood kinetic model. Starting by this point, a preliminary mathematical model for the reactor description was performed through mass balance for cyclohexane as functions of bed-height. A schematic representation of the elementary fluidized bed volume is reported in Figure 1, where is considered an orthogonal monometric system  $x y z$  with the plan  $\Pi xy$  coinciding with the cross section of the reactor, and  $z$  axis with reactor height. We assumed also that photons enter into the reactor through the surfaces at  $x=0$  and  $x=L$  (where  $L$  is the reactor thickness), and that the value of incident light intensity is the same along  $z$  axis, with a radiant flux  $\phi_0$ , variable only along  $x$  axis.



**Figure1 Sketch of the elementary fluidized bed volume.**

Taking into account that the interaction between photoexcited molybdate and adsorbed cyclohexane is the rate limiting step, the functionality in light intensity was found. Considering these factors, cyclohexane mass balance can be written as

$$\left(\frac{1}{R \cdot T}\right) \cdot v_g \frac{dC_1(x, z)}{dz} = -k_1 \cdot \frac{k_2 \cdot \phi_0(x)}{1 + k_2 \cdot \phi_0(x)} \cdot \frac{b \cdot C_1(x, z)}{1 + b \cdot C_1(x, z)} \cdot \rho_{app}$$

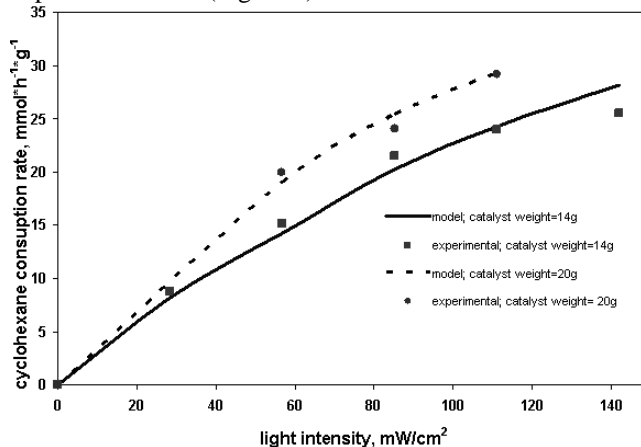
where  $C_1$  is cyclohexane concentration,  $k_1$  and  $k_2$  are the kinetic constants,  $b$  is the adsorption coefficient of cyclohexane,  $T$  is the reaction temperature and  $\rho_{app}$  is the apparent density of fluidized catalyst.

The boundary condition for mass balance is:

for  $z = 0$  and  $\forall x$   $C_1 = C_1^0$ ; where  $C_1^0$  = initial cyclohexane concentration.  $\forall z$  the average cyclohexane concentration in the cross section is calculated by integrating the concentration profile in the cross section. Radiation transmission throughout fluidized photocatalysts as a function of reactor thickness can be modelled using the Beer-Lambert's law.

The equations were solved by the Euler iterative method by fitting experimental data conversions as a function of

the light intensity for a catalyst weight of 14g. The accuracy of the developed model was tested by comparing the calculated cyclohexane consumption rate with the experimental results at different incident light intensity and for a catalyst weight of 20g. In both cases the calculated values are in good agreement with the experimental data (Figure 2).



**Figure2 Comparison between model calculations and experimental data of cyclohexane reaction rate as function of incident light intensity.**

## Conclusions

Factors affecting the kinetic of photocatalytic oxidative dehydrogenation of cyclohexane to benzene in a two dimensional fluidized bed reactor were analyzed. A mathematical modelling has been performed by using the Langmuir-Hinshelwood kinetic model for cyclohexane concentration. Taking into account that the interaction between photoexcited molybdate and adsorbed cyclohexane is the rate limiting step, the functionality in light intensity was found, with a very good agreement between mathematical model prediction and experimental data as a function of light intensity. On the basis of these results, the accuracy of the model will be tested also with experimental data obtained as a function of initial cyclohexane concentration and as a function of the reactor thickness.

## References

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