Improved photocatalytic synthesis of benzene by oxidative dehydrogenation of cyclohexane on MoO$_x$/TiO$_2$-Al$_2$O$_3$ catalysts

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The photocatalytic synthesis of benzene by oxidative dehydrogenation of cyclohexane has been studied in a fluidized bed reactor. In order to improve the fluidization behavior titania-alumina mixed supports have been prepared by sol-gel technique and then impregnated with molybdate solution. Titania-alumina supported showed good fluidization properties and improved cyclohexane conversion in photocatalytic tests with respect to MoO$_x$/TiO$_2$–alumina physical mixtures. High benzene selectivity was obtained and during illumination time no catalyst deactivation was observed. The effect of catalyst sulphate content on the photoactivity has been evaluated. It has been found that the best photocatalytic performances of MoO$_x$/TiO$_2$-Al$_2$O$_3$ catalysts at 10 wt % of MoO$_3$ are obtained in the presence of 1 wt % of sulphate.

1. Introduction

Photocatalysis has been mostly investigated for the treatment of environmental contaminants by both in water and air streams (Ju et al., 2002). Only recently photocatalytic processes have been taken into account for applications in the synthesis of chemicals from hydrocarbon feedstocks. With regard to oxidation processes, the research is focused on novel catalysts capable of inducing oxofunctionalization of hydrocarbons. The development of selective catalysts, especially in the presence of oxygen gas as reactant, plays a key role to this purpose.

Recently we have shown that cyclohexane is selectively photooxidised on MoOx/TiO$_2$ catalysts in the presence of gaseous oxygen at 35°C under UV illumination in gas-solid fixed bed reactor (Ciambelli et al., 2005a). Significant enhancement of catalytic activity was achieved with a fluidized bed photoreactor. Since titania belongs to C group of Geldart distribution, physical mixtures with α-Al$_2$O$_3$ were used to enhance the catalyst fluidizability (Ciambelli et al, 2006).

An alternative to the physical mixing of titania based catalyst and α−Al$_2$O$_3$ is to realize TiO$_2$-Al$_2$O$_3$ mixed oxides catalytic supports.

Mixed oxides have been used in photocatalytic processes mainly for environmental applications. Two kinds of chemical vapour deposition approaches have been employed for the preparation of the photocatalyst of titanium dioxide supported on alumina (Zhang et al., 2005). One was simultaneous deposition and calcination (one-step process); the other was preliminary gas impregnation of the support followed by a decomposition step (two-step process). The results of characterization indicated that the structure of the support was destroyed by a two-step process because of pore blocking.

It was found that the one-step process resulted in a superior photocatalyst; this was attributed to higher external surface concentration and more perfect crystalline structure of TiO_2. Titania, synthesized through a sol-gel procedure with acetylacetone chelating agent, was immobilized on γ-Al_2O_3 and deposited together with photoreduced Ag (Chen et al., 2005) for decolourization of methyl orange. The photoactivity of TiO_2/γ-Al_2O_3 was affected by the H_2O/Ti molar ratio applied in the sol-gel process. The preparation of two sets of polycrystalline photocatalysts prepared by supporting TiO_2 (anatase) on TiO_2 (rutile) or Al_2O_3 is reported (Loddo et al., 1999). The powders were prepared by a wet impregnation method using titanium(IV) isopropylate. Both sets of TiO_2 (anatase) supported samples resulted photoactive and the photoactivity toward 4-nitrophenol photodegradation increased by increasing the content of anatase phase.

In this work, in order to improve the fluidization behavior of titania, titania-alumina supports have been prepared, impregnated with Mo and tested in photocatalytic cyclohexane oxidative dehydrogenation. The effect of catalyst sulphate content has been evaluated.

1. Experimental

1.1 Catalysts preparation and characterization

Anatase titania samples (DT51, PC100, PC105 and PC500 provided by Millemium Chemicals) containing different sulphate load were impregnated with an aqueous solution of ammonium heptamolybdate $(NH_4)_6$ Mo_7O_{24}·$4H_2O$, dried at 120°C and calcined in air at 400°C for 3 hours.

Titania-alumina supports (PC500Al, PC105Al, PC100Al and DTAl) were prepared by dispersing the parent titania powder in a boehmite sol (10 wt% of Condea Pural in bydistilled water, pH< 2 by HNO_3). The sol was gelled by slight heating until it was too viscous to stir. The gel was thus dried at 120°C for 3 hours and calcined at 500°C for 2 hours. After calcination the solid was crushed and sieved to 50-90 μm size fraction. The obtained support (30 wt% Al_2O_3) was impregnated with $(NH_4)_6Mo_7O_{24}$ solution, dried and calcined at 400°C. Specific surface area of the supports and of molybdenum based catalysts was evaluated by nitrogen adsorption measurements at -196 °C. Thermogravimetric analysis coupled with mass spectrometry (TG-MS) of catalyst samples in air flow was carried out in order to evaluate the sulphate content as described by Ciambelli et al. (2006a).

1.2 Photocatalytic tests

The design and geometric characteristics of the used fluidized bed photoreactor are reported elsewhere (Ciambelli et al., 2006b).

Photocatalytic tests were carried out feeding 830 (stp)cm³/min nitrogen stream containing 1000 ppm cyclohexane, 1500 ppm oxygen and 1600 ppm water with oxygen/cyclohexane and water/cyclohexane ratio respectively equal to 1.5 and 1.6. The reaction temperature was 120°C. In order to obtain effective fluidization physical mixtures of MoO_x/TiO_2–alumina at different percentage of alumina were tested. The optimal mixture was made by 14g of catalyst and 63 g of α–Al_2O_3 (diluted bed). In the case of titania-alumina catalyst, the reactor was loaded with 14 g of sample without dilution (undiluted bed). As UV light sources two (EYE MERCURY LAMP 125 W, Philips) lamps with spectrum emission centred at 365 nm, were used. The gas

composition was continuously measured by an on-line quadrupole mass detector (TraceMS, ThermoElectron) and a continuous CO-CO_2 NDIR analyser (Uras 10, Hartmann & Braun).

2. Results and discussion

Table 1 List of catalysts and their characteristics

Catalyst	Support	Nominal MoO_3 wt %	SO_3 wt %	S.S.A, m^2/g	MoO_3 surface density, $\mu mol/m^2$	SO_4^{2-} surface density, $\mu mol/m^2$
17MoPC500	TiO_2	16.6	0.48	241	3.59	0.21
6MoPC105	TiO_2	5.9	0.33	87	3.53	0.39
6MoPC100	TiO_2	6	1.2	88	3.55	1.42
5MoDT2	TiO_2	4.7	1.8	68	3.57	2.76
19MoPC500Al	TiO_2-Al_2O_3	19	0.26	280	3.53	0.13
10MoPC105Al	TiO_2-Al_2O_3	10	0.25	150	3.47	0.17
10MoPC100Al	TiO_2-Al_2O_3	10	0.78	148	3.52	0.55
10MoDTAl	TiO_2-Al_2O_3	10	1.4	147	3.54	0.99

The nominal MoO_3 and sulphate content (evaluated by TG-MS analysis) together with the specific surface area (S.S.A) of the photocatalysts are reported in Table 1. The SO_4^{2-} and MoO_3 surface density were evaluated on final S.S.A obtained after calcination for each catalyst. All catalysts were designed to reach similar MoO_3 surface density (3.5 $\mu mol/m^2$). Photocatalytic tests showed that benzene was the main reaction product formed during irradiation. The typical trend for Mo supported on TiO_2 tested by diluition with α-Al_2O_3, is reported in Figure 1 with reference to 6MoPC100. When the lamps were switched on, the cyclohexane conversion immediately increased reaching a steady state value corresponding to about 8% cyclohexane conversion after about 7 minutes. The outlet concentration of benzene progressively increased up to 75 ppm after about 10 minutes. Similar behaviour is obtained for Mo supported on TiO_2-Al_2O_3 (Figure 2) with reference to 10MoDTAl. Steady state values were about 13% and 127 ppm for cyclohexane conversion and benzene concentration, respectively. A similar trend was shown by cyclohexene concentration although 3 ppm maximum value was reached. No deactivation of catalyst was observed during photocatalytic tests. Figure 3 displays cyclohexane conversion and benzene obtained with mixed TiO_2-Al_2O_3 based catalyst (undiluted bed) and TiO_2 based catalyst (diluted bed) as a function of the surface sulphate density. Both cyclohexane conversion and benzene selectivity increased with the sulphate density, evidencing that the selectivity properties of photocatalysts are influenced by the presence of active phases, sulphate and molybdate species on the supports, as previously shown (Ciambelli et al., 2005b).
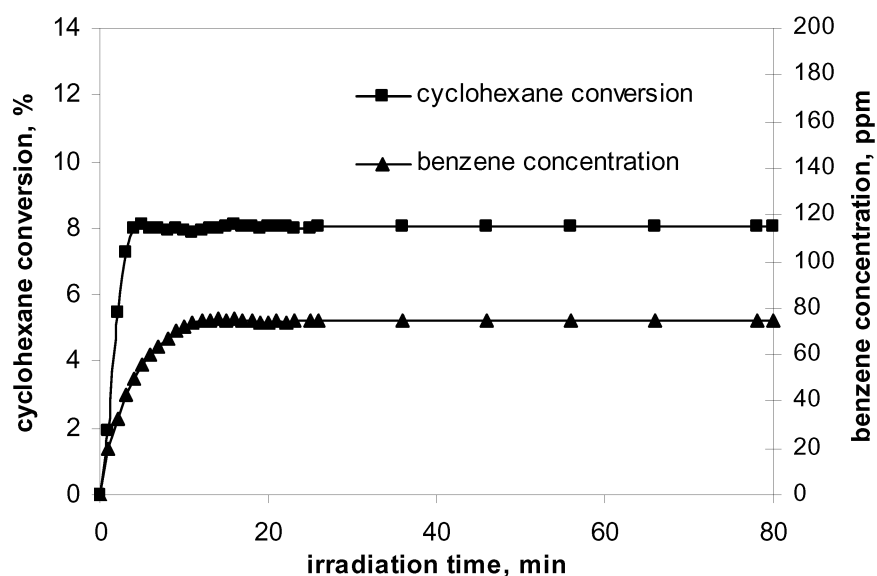
Figure 1 Cyclohexane and benzene outlet concentration as a function of irradiation time (6MoPC100 catalyst)
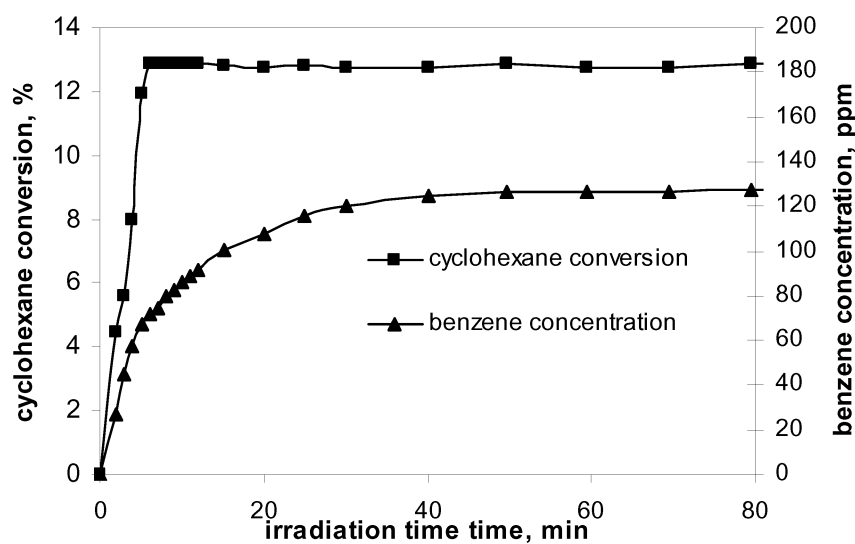

Figure 2 Cyclohexane and benzene outlet concentration as a function of irradiation time (10MoDTAlcatalyst)

It is believed that the presence of sulphate decreases the band gap and helps the transfer and separation of photogenerated electrons and holes (Gomez et al., 2003). Moreover, at similar sulphate surface density, both cyclohexane conversion and benzene selectivity obtained with undiluted bed are better than with diluted bed. This result is likely due to a better utilization of UV light than through $\alpha-Al_2O_3$ diluted bed.
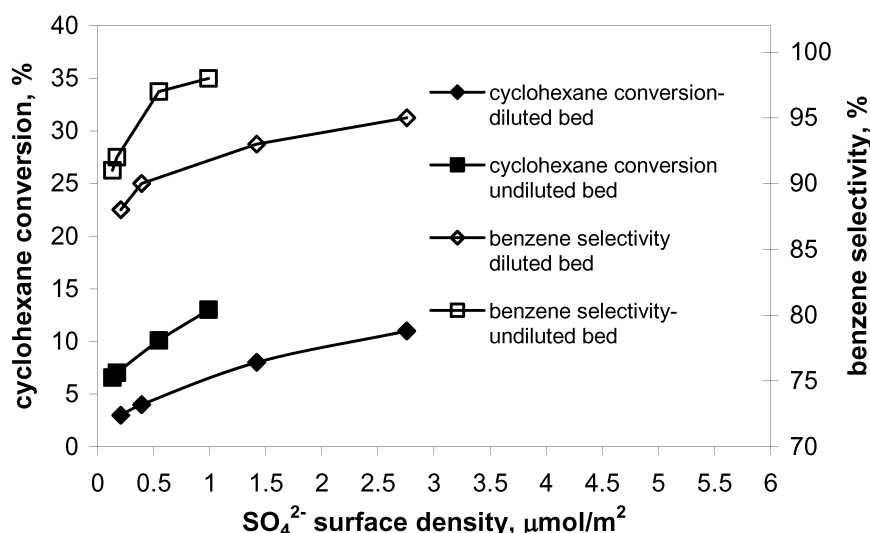
Figure 3 Cyclohexane conversion and benzene selectivity as a function of sulphate surface density

Beyond benzene, cyclohexene and carbon dioxide were detected as by-products, as shown in Figure 4. CO_2 in very low concentration was formed only with diluted bed, indicating a better exposition to UV light of bare titania, responsible for CO_2 formation (Ciambelli et al.,2005a), with respect to undiluted bed. It can be seen that cyclohexene selectivity decreased with sulphate surface density, likely related to the increase of catalysts acidity that enhances the adsorption of cyclohexene on the catalyst surface (Navio et al., 1996), favouring its conversion to benzene. From Figure 4 it is also noted that CO_2 selectivity decreased with the sulphate content. This behaviour may be explained taking into account the reaction mechanism of gas-solid photocatalytic oxidation of cyclohexane to CO_2 on titania catalyst (Einaga et al., 2002). In their scheme the surface hydroxyl groups exhibit a major role in the photoreaction process by trapping the charge transfer to produce very reactive surface hydroxyl radicals. The presence of sulphate, grafted to the surface by reaction with hydroxyl groups, decreases their surface concentration. In addition it is worthwhile to note that the rehydroxylation of the catalyst surface is an essential step for the activity of titania toward cyclohexane total oxidation. Xie et al. (2004), studying gas-solid photocatalytic oxidation of heptane on sulphated and unsulphated titania in the presence of water vapour, found that the presence of SO_4^{2-} may be detrimental to the rehydroxylation ability of the catalyst.
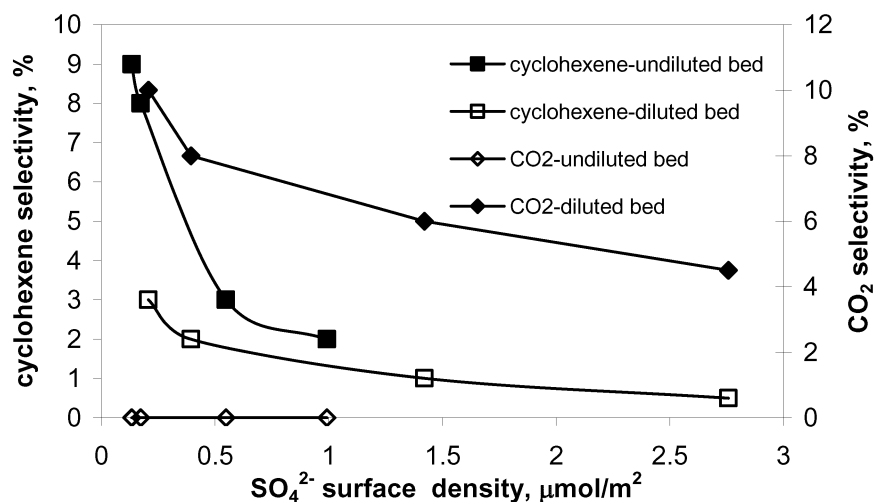
Figure 4 Cyclohexene and CO₂ selectivity as a function of sulphate surface density

3. Conclusions

The photocatalytic synthesis of benzene by oxidative dehydrogenation of cyclohexane was studied in a fluidized bed reactor. Catalysts prepared on titania-alumina mixed support improved cyclohexane conversion and benzene selectivity with respect to MoO_x/TiO_2–alumina physical mixtures. Moreover, the activity and selectivity of photocatalysts are influenced by the presence of both sulphate and molybdate species.

4. References

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