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Sustainable Gas Phase Selective Photocatalytic Oxidation of Cyclohexane on $MoO_x/TiO_2/SiO_2$ catalysts

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Gas phase selective photocatalytic oxidation of cyclohexane was studied in a two dimensional fluidized bed reactor on MoO_x catalysts supported on grafted TiO_2/SiO_2. The influence of sulphate and Mo loading was evaluated. Photocatalytic tests showed that benzene was the main reaction product formed during irradiation with together CO_2 and cyclohexene as by products.

Depending on the TiO_2, Mo and sulphate loading, an enhancement of the activity and catalysts stability occurred during irradiation. $MoO_x/TiO_2/SiO_2$ samples showed a higher photocatalytic activity with respect to MoO_x/TiO_2-Al_2O_3. This behaviour was attributed to the better transmission of UV light through SiO_2 than through Al_2O_3 and the lower absorption of the radiation.

1. Introduction

Heterogeneous photocatalysis can be an effective alternative to removal bacteria (Rizzo et al., 2014) and organic pollutants such as methyl-ethyl ketone (Hajaghazadeh et al., 2014), cyclohexane (Murcia et al., 2013), methylene blue (Sannino et al., 2013a) and NO_x (Sannino et al., 2013b) or obtain partial oxidation products in mild conditions such as styrene (Sannino et al., 2013c), acetaldehyde (Sannino et al., 2013d) and cyclohexanol or cyclohexanone (Sannino et al., 2013e). Ciambelli et al. showed that cyclohexane is selectively photoxidised on MoO_x/TiO_2 catalysts in the presence of gaseous oxygen at 35 °C under UV illumination in gas-solid fixed bed reactor (Ciambelli et al., 2008). Significant enhancement of catalytic activity was achieved with a fluidized bed photoreactor (Palma et al., 2010).

Titania is typically a solid of group C in the particle distribution proposed by Geldart (1972). This type of particles exhibit cohesive tendencies and as the gas flow is further increased, bubbling regime is developed and the photoreactor acts as a “ratholing”; the gas opens bypass channels that extend from the gas distributor to the upper edge of the fluidized bed. If channels are not formed, the whole bed expands and lifts up as a piston. At higher velocities or with mechanical agitation or vibration, this type of particle will be fluidized but with the appearance of clumps or large clusters of particles. These phenomenons play a negative role on particle light exposition.

For testing Mo-titania catalyst, in order to obtain good fluidization, physical mixtures with α-Al_2O_3 was used to enhance the catalyst fluidizability (Ciambelli et al., 2007), since α–Al_2O_3 is a solid of group A. When gas is passed upward through a bed of particles of groups A, B, or D, friction causes a pressure drop and the fluidized bed is expanded. As the gas velocity is increased, the pressure drop increases until it equals the weight of the bed divided by the cross-sectional area. This velocity is called minimum fluidizing velocity, U_{mf}. When this point is reached, the bed of group A particles will expand uniformly until at some higher velocity gas bubbles will form (minimum bubbling velocity, U_{mb}). This process can avoid the appearance of clumps or clusters of titania particles and improve light exposition.

As alternative, mixed oxides, such as TiO_2-Al_2O_3, are useful supports for Mo-species, (Palma et al., 2010). TiO_2-Al_2O_3 supports for MoO_x species showed good fluidization properties and higher cyclohexane conversion in presence of UV irradiation (Palma et al., 2010). To further increase the performance of the gas-phase photocatalytic fluidized bed reactor, TiO_2 based catalysts could be directly supported on material transparent to ultraviolet radiation. Interesting examples are TiO_2/SiO_2 catalysts that are considered advanced support materials able to support pure TiO_2 (Sannino et al., 2013f).

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In this work gas phase photocatalytic selective oxidation of cyclohexane was studied with MoO_x catalysts supported on grafted TiO_2 on SiO_2. The influence of TiO_2 sulphate and Mo loading was evaluated.

2. Experimental

2.1 Catalysts preparation and characterization

Supports of silica coated with TiO_2 was prepared in a grafting procedure, starting from titanium isopropoxide dissolved in toluene and a commercial silica followed by calcination at 500 °C for 8 h (Cozzolino et al., 2007). TiO_2/SiO_2 samples were added to an aqueous solution of ammonium sulphate, dried at 120 °C and calcined in air at 300 °C for 3 h. A second impregnation with an aqueous solution of ammonium heptamolybdate was performed, followed by calcination at 400 °C for 3 h to obtain $MoO_x/TiO_2/SiO_2$ catalysts. Catalysts were characterized with different techniques. Specific surface area was measured by N_2 adsorption measurement at -196 °C with a Costech Sorptometer 1040 after pretreatment at 150 °C for 30 min in He flow (99.9990 %).

Laser Raman spectra were obtained at room temperature with a Dispersive MicroRaman (Invia, Renishaw), equipped with 633 nm diode-laser, in the range 100-2,500 cm^{-1} Raman shift. Thermogravimetric analysis (TG-MS) of powder samples was carried out in air flow with a thermoanalyzer (Q600, TA) in the range 20–1,100 °C at 10 °C/min heating rate.

UV-Vis reflectance spectra were recorded with a Perkin Elmer spectrometer Lambda 35. Equivalent band gap determinations were obtained from Kubelka-Munk theory (Ciambelli et al., 2007) by plotting $[F(R\infty)\cdot h\nu]^2$ vs $h\nu$ and calculating the x intercept of a line through $0.5 < F(R\infty) < 0.8$. X-ray diffraction (XRD) was carried out using an X-ray microdiffractometer Rigaku D-max-RAPID, using Cu-Kα radiation.

2.2 Photocatalytic tests

Photocatalytic tests were carried out feeding 830 Ncm^3/min He stream containing 0.1 % cyclohexane, 0.15 % oxygen and 0.16 % water. Photocatalytic fluidized bed reactor was illuminated by two UVA-LED modules, positioned in front of each Pyrex windows (40 x 50 mm). The light intensity was regulated at 100 mW/cm^2. Each UVA-LED array consisted of 20 pieces of UVA-LEDs (provided by Nichia Corporation) emitting at 365 nm. To control the reaction temperature at 120 °C, an electrical heater and a thermocouple were immersed within the catalytic bed. The catalyst weight was 7 g.

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, ABB). UV light was switched on after the reaching of adsorption equilibrium of cyclohexane on the catalyst surface.

3. Results and discussion

3.1 Catalysts characterization

The list of supports and catalysts with their TiO_2, MoO_3 and SO_3 content are reported in Table 1. The values of specific surface area (SSA) and band-gap energy are also displayed. MoO_3 and SO_3 percentage were evaluated on the effective TiO_2 loading in TiO_2/SiO_2 sample.

Table 1: Catalysts and their characteristics

Catalyst	TiO_2 wt %	MoO_3 wt %	SO_3 wt %	SSA m^2/g	E_{bg} eV
TiSi1	10	0	0	380	3.5
TiSi2	18.8	0	0	340	3.4
8Mo2STiSi1	10	8	2	350	3.5
16Mo4STiSi1	10	16	4	345	3.1
8Mo2STiSi2	18.8	8	2	321	3.3
16Mo4STiSi2	18.8	16	4	314	3.2

The specific surface areas decreased with TiO_2 loading for the samples TiSi1 and TiSi2. The same effect is obtained after the addition of SO_3 and MoO_3 on the support surface. No significant effect on the band gap energy values was found. XRD analysis (not reported) did not show signals related to molybdenum species, but only diffraction patterns related to TiO_2 in anatase phase, underlining that a very good dispersion of MoO_x species was obtained. Figure 1a and 1b show the Raman analysis of all the prepared photocatalysts. With respect to TiO_2/SiO_2 supports, the presence of Mo_x species caused Raman signals in the range 900–1,100 cm^{-1}. Specifically, Raman spectra show main bands at 955 cm^{-1} on 8Mo2STiSi1 and

8Mo2STiSi2, and at about 963 cm^{-1} on 16Mo4STiSi1 and 16Mo4STiSi2. These bands are attributed to polymolybdate coordinated with the support surface and Polymerization degree of these species increases with the Mo loading (Ciambelli et al., 2008). The absence of bulk molybdena bands at 819 and 995 cm^{-1} (Ciambelli et al., 2008) for all Mo-based catalysts confirms the absence of MoO_3 crystallites.

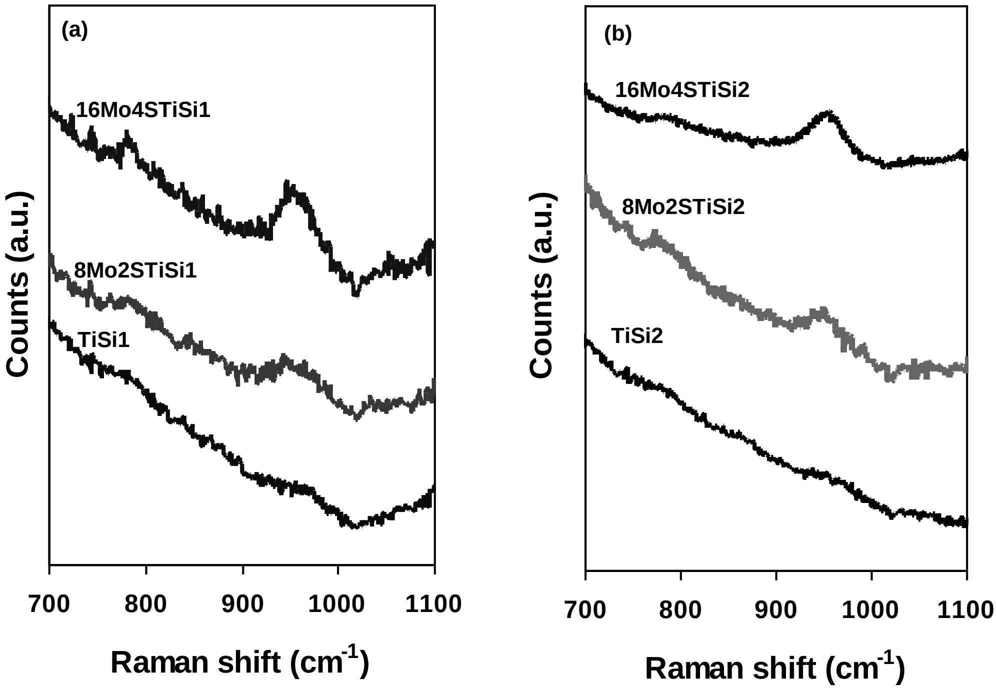

Figure 1: Raman spectra of photocatalysts

3.2 Photocatalytic activity tests

Preliminary tests carried out in absence of UV light evidenced that no reaction occurred in dark conditions. Figure 2 shows cyclohexane consumption rate with together benzene and CO_2 formation rate obtained over all the photocatalysts under UV irradiation. On TiSi1 and TiSi2, CO_2 was the only product detected in the gas phase (100 % selectivity). Photocatalytic tests on $MoO_x/TiO_2/SiO_2$ catalysts evidenced that benzene was the main reaction product formed during irradiation with together CO_2 and cyclohexene as by products. On 8Mo2STiSi2, the cyclohexane consumption rate reached a maximum value after about 5 min, and then activity decreased during irradiation. A completely different behaviour was found on 8Mo2STiSi1. In this case the cyclohexane consumption rate increased to steady state value without deactivation phenomena. Moreover, on 8Mo2STiSi2 the formation rate of benzene progressively increased reaching a maximum value of about 9 μmol h^{-1} g^{-1} after 9 min and then decreased. Instead, on 8Mo2STiSi1 benzene formation rate progressively increased reaching a steady state value of about 8.5 μmol h^{-1} g^{-1} (corresponding to a benzene selectivity of 96 %) after about 12 min.

TG-MS analysis in air flow of 8Mo2STiSi2 after photocatalytic test (Figure 3) evidenced the presence of carbonaceous species adsorbed on the catalyst surface that could explain the loss of photoactivity observed during irradiation. Deactivation phenomena were not observed when MoO_3 and SO_3 loading were increased to 16 and 8 wt % respectively. In fact, photocatalytic performances were strongly enhanced on 16Mo4STiSi1 and the increase of Mo loading determined an increase of photocatalytic activity. In particular, on 16Mo4STiSi1, steady state cyclohexane consumption rate was about 42 μmol h^{-1} g^{-1} (97 % benzene selectivity), higher than that obtained (17 μmol h^{-1} g^{-1}) on an optimized formulation for MoO_x/TiO_2-Al_2O_3 catalysts, where the support was obtained by sol-gel technique (Palma et al., 2010). The higher photoactivity of 16Mo4STiSi1 with respect to 16Mo4STiSi2 is likely attributed to the superior SSA of the first one. This result confirms what found before (Ciambelli et al., 2009), where the improved activity was attributed to the better transmission of UV light through SiO_2 than through Al_2O_3.

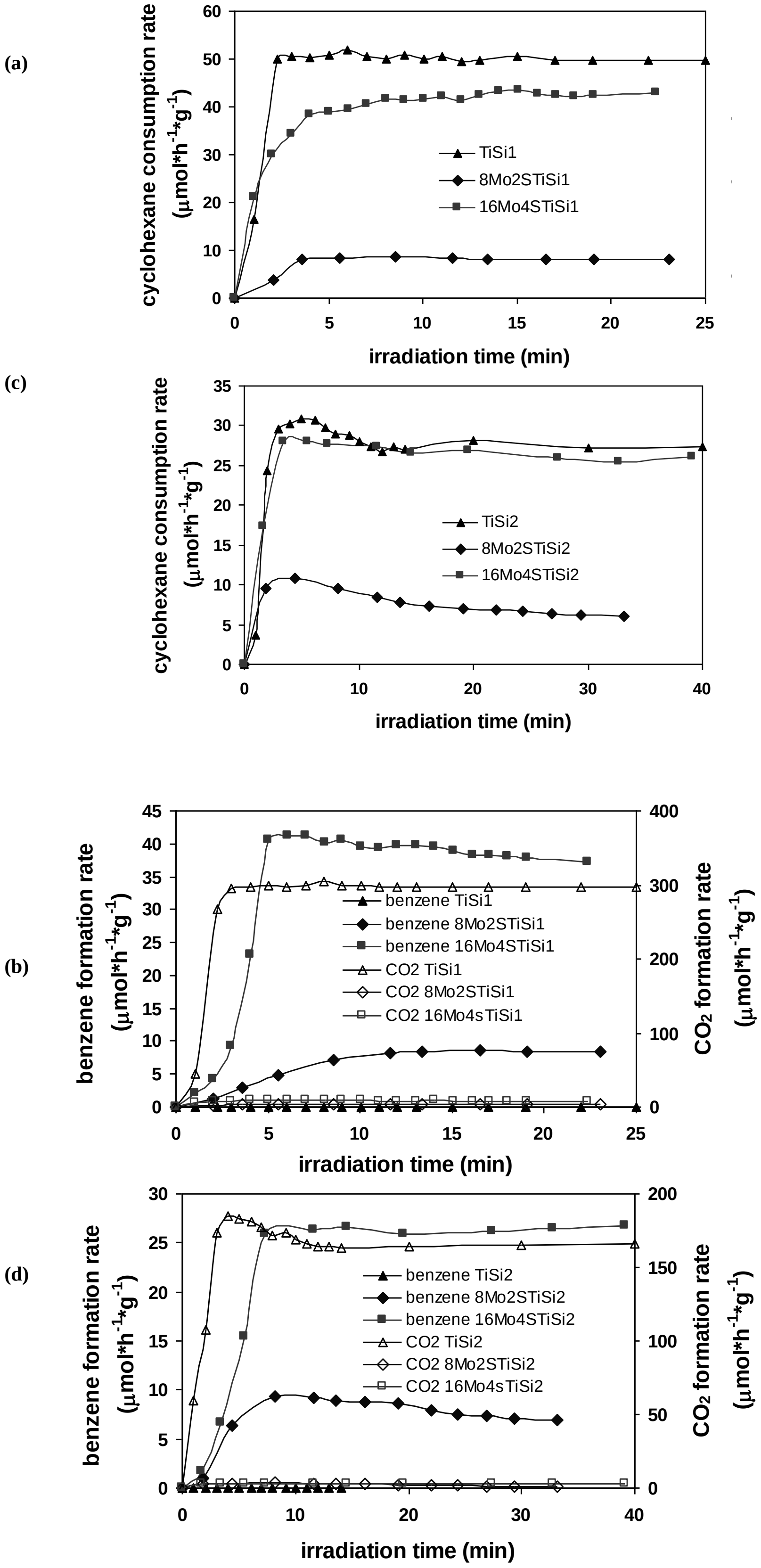

Figure 2: Cyclohexane consumption rate, benzene and CO_2 formation rate as a function of irradiation time

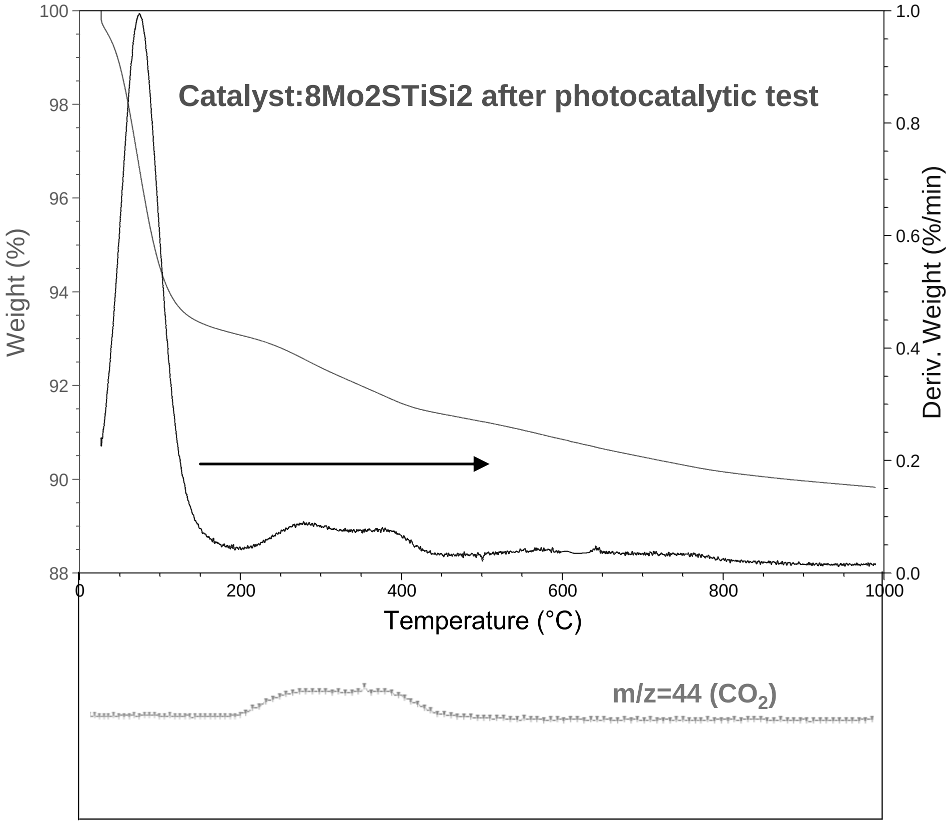

Figure 3: TG-MS of 8Mo2STiSi2 sample after photocatalytic test

4. Conclusions

Photocatalytic selective oxidation of cyclohexane to benzene was studied $MoO_x/TiO_2/SiO_2$ in a fluidized bed reactor. Photocatalytic tests showed that benzene was the main reaction product formed during irradiation with together CO_2 and cyclohexene as by products. Depending on the TiO_2, Mo and sulphate loading, an enhancement of the activity and catalysts stability occurred during irradiation.

$MoO_x/TiO_2/SiO_2$ samples showed a photocatalytic activity higher than MoO_x/TiO_2-Al_2O_3. This behaviour was attributed to the better transmission of UV light through SiO_2 than through Al_2O_3.

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