An Operando-IR Study of Photocatalytic Reaction of Methanol on New BEA Supported TiO_2 Catalyst

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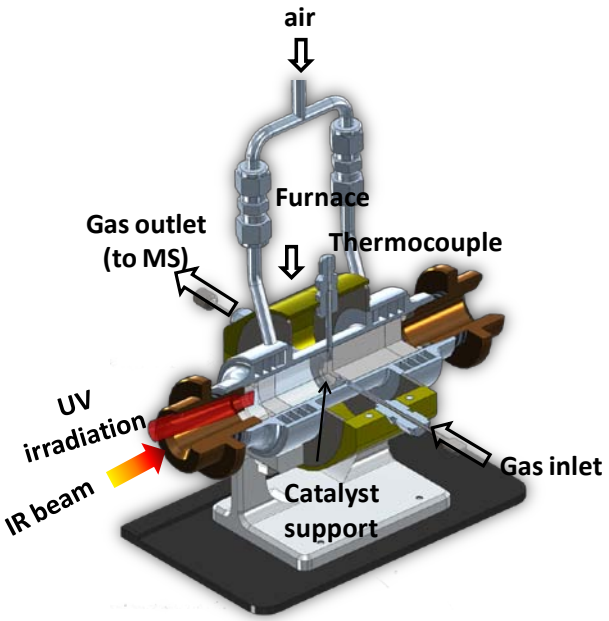
The growing concern in the general public as well as the increased severity of air control regulations give special interest to the removal of Volatile Organic Compounds (VOC). One of the key features for such removal is the use of heterogeneous catalysts, largely used for the control and treatment of exhaust gases in the chemical and car industries. The reaction on the catalyst can be induced by heating, or by UV light when using a photocatalyst, with advantages such as low cost, excellent efficiency at room temperature and low environmental impact.

In order to study and improve the catalyst efficiency, it is important to have quantitative and mechanistic information of the catalytic reaction. The parameters of the reaction (reactive compositions, temperature, flux rate...) could be play a crucial role on the catalyst reactivity and must be controlled in order to prove the effective role of these parameters. For these reasons, operando techniques could be ideal candidates to study a catalytic reaction; it allows monitoring events taking place on and inside the catalyst in real time. Infrared spectroscopy (IR) is for that purpose very appropriate since it is fast and sensitive.

In this work, a new operando setup was used to study the photocatalytic oxidation of methanol in gas phase using a new BEA zeolite supported TiO_2 (BEA-Ti) photocatalyst. Following the photocatalytic reaction with time resolved IR spectroscopy coupled to mass spectrometry allowed a quantitative and mechanistic study. Two types of photocatalyst have been investigated TiO_2 (P25-Degussa) and BEA supported TiO_2 (BEA-Ti). It highlights the interesting reactivity of BEA-Ti compound. With only ~10 wt.% of incorporated TiO_2, BEA-Ti showed a relatively high efficiency (50%) compared to TiO_2. By considering the mass weight of TiO_2, the reactivity of BEA-Ti was 5 times higher than that of TiO_2–P25. For comparison, BEA zeolite has been also investigated as photocatalyst. It did not show any photooxidation activity. The selectivity of TiO_2 and BEA-Ti photocatalysts was found to be different. While the major reaction observed in the case of TiO_2 was the photocombustion, the formation of methyl formate species in case of BEA-Ti contributed to ~50% of the photoxidation (vs ~50% of photocombustion reaction). The

temperature has a direct impact on the reactivity (and selectivity) of the photooxidation especially for BEA-Ti. Indeed, for TiO_2 photocatalysts high temperatures (> 443 K) favour the chemisorption and lead to a decrease in the reactivity. In contrary, for BEA-Ti, the increase of the temperature increases the conversion of methanol and the reactivity.



Scheme 1 The sandwich IR-reactor cell modified for UV catalysis study.