

Zeolite Effect on the Oxidation of Hydrocarbons with Irradiated TiO₂ Semiconductor

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The effect of an acidic zeolite on the photocatalytic oxidation of isopropylbenzene and α -methylstyrene over irradiated TiO₂ leads to either an increase or a decrease in oxidation rate depending on the substrate but, in both cases, an increase in selectivity is observed.

Heterogeneous photocatalysis, applied to the oxidation of organic compounds at room temperature using irradiated semiconductor materials and molecular oxygen has become a rapidly growing area of research in the last few years.¹ The interest in this field of study arises from synthetic, mechanistic or environmental applications.

Among the hydrocarbons, toluene and alkyltoluenes^{2,3} and various saturated or partially unsaturated model cyclic compounds have already been investigated over TiO₂^{4,5} and modified TiO₂ (Pt or Mo deposition,^{6,7} iron-doped⁸) as the catalyst.

Photoreactions of organic molecules adsorbed on solid surfaces have also attracted considerable attention in recent years. Zeolites, microporous solids with acidic and shape selective properties are used in such reactions and an intrazeolite photochemistry has been developed.^{9,10} However, the use of zeolites has not been attempted in heterogeneous photocatalytic oxidation using irradiated semiconductor materials.

Our recent results prompt us to report the present work which is, to our knowledge, the first attempt involving both zeolite and semiconductor in photocatalytic oxidation.

Two aromatic compounds were chosen: isopropylbenzene and α -methylstyrene. The zeolite used in this study was a HY-faujasite-type zeolite ZF 520 (HY20) with the ratio Si/Al = 20 supplied by Zeocat. In a typical experiment the zeolite HY20 (0.3 g) was activated at 500 °C overnight before use. The activated zeolite was added to the organic compound (1 g) in dichloromethane (3 ml) and stirred for 3 h at room temperature. Then, the solvent was evacuated under reduced pressure. The substrate-impregnated zeolite was added to a magnetically stirred TiO₂ (Degussa P25 0.3 g)-neat acetonitrile (330 ml) suspension and irradiated with a HPK 125 W mercury lamp ($\lambda = 330$ nm) under an oxygen flow (120 cm³ min⁻¹). For reactions in the absence of zeolite, the substrate was directly added to the TiO₂-acetonitrile suspension. Samples were taken and analysed by gas liquid chromatography (OV1-capillary column 25 m) and GC-MS. The

Table 1 Photooxidation of hydrocarbons with TiO₂ and with TiO₂ and zeolite

Substrates	Isopropylbenzene		α -Methylstyrene	
	Conversion (%)	Products (%)	Conversion (%)	Products (%)
TiO ₂	38 (after 96 h)	Acetophenone 84 2-Phenylpropan-2-ol 16	70 (after 24 h)	Acetophenone 88 Epoxide 9 2-Phenylpropanaldehyde 3
TiO ₂ + Zeolite HY20	99 (after 72 h)	Acetophenone 98 2-Phenylpropan-2-ol 2	55 (after 24 h)	Acetophenone 100

products were identified by comparison with standard references.

Table 1 compares the results of the oxidation of the two aromatic derivatives, first over TiO₂, and then over both TiO₂ and zeolite. Oxidation of isopropylbenzene over TiO₂ alone led to acetophenone as the main product and to the tertiary alcohol, 2-phenylpropan-2-ol. Under the same conditions, the distribution of the oxidation products from α -methylstyrene has shown the formation of acetophenone as the main product and α -methylstyrene oxide and 2-phenylpropanaldehyde as secondary products. In all cases, no oxidation of the aromatic ring was detected.

Addition of the acidic zeolite led to an increased selectivity: in both cases, the amount of acetophenone was virtually quantitative. We think that the selectivity is not due to a shape selective oxidation resulting from the zeolite structure but due to an acidic effect which favours the formation of acetophenone.

Furthermore, it can be seen from the effect of time that the rate of isopropylbenzene oxidation increases whereas a decreasing rate is noticed with α -methylstyrene. These apparently opposite effects observed in the oxidation rate of isopropylbenzene and α -methylstyrene with irradiation over TiO₂ and zeolite seem to be related, in a first approach, to different mechanisms involved for these two substrates: dioxetane stabilisation by acidic zeolite in the case of

α -methylstyrene and radical cation adsorbed on the zeolite in the case of isopropylbenzene.

Work is in progress in order to elucidate the mechanism.

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