Catalytic Synthesis of 2,6-Dimethylphenol from Methanol and Cyclohexanone over Titanium Oxide-supported Vanadium Oxide Catalysts

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2,6-Dimethylphenol has been selectively synthesised from methanol and cyclohexanone in one step over a vanadia/TiO_2 catalyst.

2,6-Dimethylphenol is important in the polymer industry for engineering plastics.[1,2] Currently, the industrial synthetic method is a liquid phase process, where phenol is methylated with methanol using an Al_2O_3 catalyst. However, this process not only needs high pressure and temperature, but also produces a wide range of products, including various isomers of xylenol.[3] Here we report a new catalytic method for selectively synthesising 2,6-dimethylphenol from methanol and cyclohexanone in one step by using vanadia/TiO_2 catalysts.

The reactions were carried out in a fixed-bed system at atmospheric pressure. Mixtures of cyclohexanone and methanol (1 : 10) were fed by a syringe pump and vaporised. The vapour was diluted with nitrogen and the total flow rate was controlled to 45 ml min^{-1}. The vandia/TiO_2 catalysts were prepared by simple impregnation.[4,5] The titanium oxide was impregnated with oxalic acid solution containing ammonium vanadate (ammonium vanadate : oxalic acid = 1 : 2). The vanadium oxide content (wt%) was based on the concentration of the vanadate anion in the processing solutions. After impregnation, the catalysts were dried in air at 110 °C for 24 h. All the catalysts were heated in air for 6 h at 500 °C before the reaction. TiO_2, the support, is an anatase type and has a BET surface area of about 50 m^2g^{-1} before and after calcination at 500 °C. All the vanadia/TiO_2 catalysts are characterised by a BET surface area close to that of TiO_2, within a range of 43–45 m^2g^{-1}.

A decrease in the conversion rate of cyclohexanone during the initial reaction period was observed for all the catalysts used but stable activities were obtained within a few hours. Almost all the excess methanol was recovered, together with a small amount of methane, after the reaction. TiO_2 shows no activity for the formation of 2,6-dimethylphenol but yields 1-methoxycyclohexene and 1,1-dimethoxycyclohexane as main products, while as vanadia is loaded, it shows a reasonable activity for the formation of 2,6-dimethylphenol. The activities of the catalysts strongly depend on the concentration of vanadia. The activity and selectivity to 2,6-dimethylphenol initially increase with the amount of vanadium. Excess addition, however, results in a decrease in the selectivity to 2,6-dimethylphenol, owing to the formation of alcohols, *e.g.* cyclohexanol, 2-methylcyclohexanol and 2,6-dimethylcyclohexanol. The optimum results for conversion and selectivity were obtained for vanadia (10 wt%)/TiO_2.

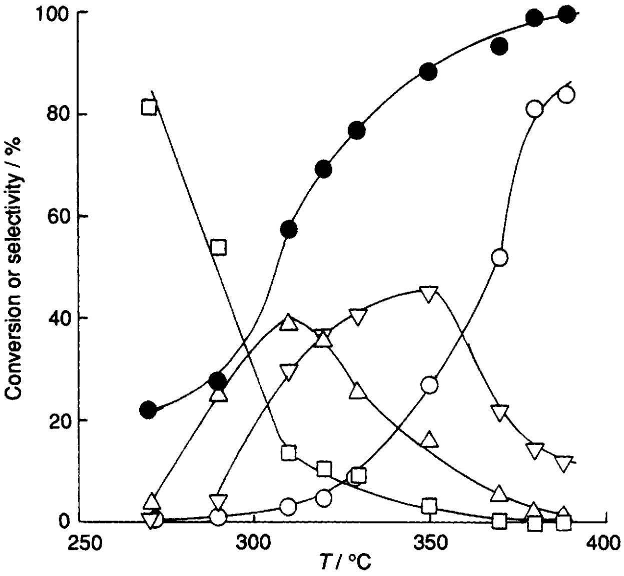

Fig. 1 The conversion of cyclohexanone, and the selectivities of 1-methoxycyclohexene, 2-methylcyclohexanone, 2,6-dimethylcyclohexanone and 2,6-dimethylphenol as a function of the reaction temperature. ● conversion, □ 1-methoxycyclohexene, △ 2-methylcyclohexanone, ▽ 2,6-dimethycyclohexanone, ○ 2,6-dimethylphenol. Catalyst: vanadia (10 wt%)/TiO_2; packing density: 0.9 g ml^{-1}; mass: 1 g. Reactant mixture: methanol 31%, cyclohexanone 3.1%, remainder nitrogen, flow rate: 45 ml min^{-1}.

The reaction over vanadia/TiO_2 catalysts selectively yields 2,6-dimethylphenol with minor amounts of 1-methoxycyclohexene, 2-methylcyclohexanone and 2,6-dimethylcyclohexanone at high conversion. Fig. 1 illustrates the cyclohexanone conversion, and the selectivities of 1-methoxycyclohexene, 2-methylcyclohexanone, 2,6-dimethylcyclohexanone and 2,6-dimethylphenol as a function of the reaction temperature in the reaction of cyclohexanone and methanol over vanadia (10 wt%)/TiO_2. The conversion increases with the reaction temperature, but the increasing rate of the conversion becomes smaller at higher temperatures. As seen in Fig. 1, whereas the selectivity of 1-methoxycyclohexene falls and that of 2,6-dimethylphenol increases continuously, the selectivities of 2-methylcyclohexanone and 2,6-dimethylcyclohexanone show similar properties which rise to a maximum at the conversion of 60 and 80% respectively, and then decrease with reaction temperature. The same change in product distribution was observed when the contact time was varied. These results suggest that the 2,6-dimethylphenol is formed by a consecutive reaction through 1-methoxycyclohexene, 2-methylcyclohexanone and 2,6-dimethylcyclohexanone as intermediate stages.

The conclusion that 2,6-dimethylphenol is formed *via* the path proposed is strongly supported by other separate experiments. 2,6-Dimethylphenol was selectively formed in high yield in both the reaction of 2,6-dimethylcyclohexanone and the reaction of methanol and 2-methylcyclohexanone over vanadia (10 wt%)/TiO_2 under the same reaction conditions; the selectivities were about 40 and 60% respectively. However, although 2-methylcyclohexanone was detected in the reaction of 1-methoxycyclohexene under these conditions, the yield of 2-methylcyclohexanone was very poor (<1%), but improved by addition of methanol in the reaction. In addition, labelled methanol (CD_3OD) was used in the reaction with 1-methoxycyclohexene, yielding [$^2H_3$]2-methylcyclohexanone (82%) as the main product. This result implies that the attachment of the first methyl to the cyclohexanone ring will involve two methanol molecules. These results suggest that the mechanism for the formation of 2,6-dimethylphenol, although not enitrely clear, might consist of a series of condensation, dehydration and dehydrogenation steps. It is interesting that such a multi-step reaction readily takes place on the catalyst surface.

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