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PROPENE OLIGOMERIZATION OVER TiO_2-ZrO_2 CATALYSTS

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Titania-zirconia mixed oxides may be prepared in high specific area form, and with or without nickel are active as catalysts for the oligomerization of propene. The presence of nickel favors the formation of oligomers containing more than ten carbon atoms per molecule.

Titania-zirconia preparations possess acidic surface sites whose strengths have been reported to be comparable to those of silica-aluminas.1-3) Titania-zirconia should be useful for oligomerizing light olefins, but the behavior of these catalysts in this respect has not been reported so far.

Titania-zirconia samples (Ti content in the range 25 mol% to 65 mol% TiO_2 equivalent) were prepared by decomposition in air at 300 °C to 500 °C of precipitates obtained by mixing solutions of tetraethylorthotitanate and zirconium acetylacetonate in toluene with aqueous NH_3. The NH_3 solution was added dropwise to the solution of the metal compounds with continuous stirring until a pH of 8 to 9 was reached (forward precipitation) or alternatively the solution of the metal compounds was added to the NH_3 solution (reverse precipitation). In both cases an approximately three-fold excess of NH_3 was used. After the precipitates had been aged at 25 °C for a selected period (from one to seven days) the solids were recovered by filtration and were subsequently washed with distilled water and then calcined in air at the desired temperature for at least 16 h. In some cases a transition metal (nickel is reported in the present work) was introduced by contacting the uncalcined titania-zirconia with aqueous $Ni(NO)_3$ and then washing and drying. Up to 0.4 wt % Ni could be added in this way.

Calcined catalysts were analyzed for titanium and (when present) nickel using chemical methods. In all cases it was found that precipitation was complete for both titanium and zirconium.

Propene oligomerization was carried out (conversion < 10%) using a fixed-bed tubular reactor at 300 °C and 0.78 MPa. Products were analyzed using gas chromatography.

Table 1 gives typical results of oligomerization studies for catalysts containing 63 mol% TiO_2. In the absence of nickel, dimerization of propene dominated under the conditions used. With fresh catalyst, just under 12 mass % of C_{10+} was obtained. Later this fraction fell to about half. In contrast, with nickel present, the fraction of C_{10+} increased markedly with time on stream, resulting in a high selectivity to C_{10+}. Both initial and subsequent activities (based on net propene loss) were higher with the nickel-containing catalysts.

Table 1. Activities and selectivities of TiO_2-ZrO_2 and Ni-TiO_2-ZrO_2 catalysts

	Catalyst					
	TiO_2-ZrO_2		Ni-TiO_2-ZrO_2 (0.1)[a]		Ni-TiO_2-ZrO_2 (0.4)[a]	
Products (mass %)	Time on stream (min)					
	<60	>200	<60	>800	<60	>800
C_{4+5}	21.6	7.7	9.0	9.0	26.0	2.0
C_6	63.9	84.0	47.5	14.8	49.0	19.0
C_{7+8}	3.5	2.3	4.5	3.2	11.2	0.1
C_9	0.2	0.1	15.0	0.2	11.6	7.2
C_{10+}	11.8	5.9	24.0	72.8	2.2	61.7
Production rate (g $kg^{-1}h^{-1}$)	204	91	504	180	672	102

a) Ni content (wt %). Ti content = 63 mol% TiO_2 equivalent. Calcination temperature = 300 °C. C_2 <0.1 % in all cases.

Deactivation was less rapid at the lower Ni loadings. The extent of cracking, as evident from the size of the C_{4+5} fraction, was relatively high on fresh catalysts but in general fell significantly as deactivation of the highly acidic sites occurred. In all cases the C_2 fraction (arising from cracking) was less than 0.1 wt %, which is in line with the behavior expected for acid catalysts of the type under investigation.

The C_6 fraction was a complex mixture consisting largely of methylpentenes. The composition was independent of the nature of the catalyst used and the time on stream; this suggests that oligomerization was accompanied by secondary isomerization which took place at a relatively rapid rate under the conditions used.

References

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