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Polymerization of ethylene in the presence of hydrogen over supported vanadium-magnesium catalysts

Summary — Catalyst activity was studied in a slurry polymerization of ethylene carried out over supported $VCl_4/MgCl_2$ and $VOCl_3/MgCl_2$ catalysts in relation to hydrogen concentration (0—40 mmols/L, *i.e.*, 0—2 bar) and to $Al(i\text{-}Bu)_3$ and $Al(i\text{-}Bu)_2H$, each used as cocatalyst. Hydrogen was found to reduce the activity of the catalyst by 2 to 6 times. The deactivation occurring in the presence of hydrogen was directly related to hydrogen pressure and found to be due to the hydride species of organoaluminum compounds forming in the side reaction of AlR_3 with the V-H bonds accompanied by adsorption of alkylaluminum hydride on active sites. A sequence of reactions is suggested (eqns. 2—5) to explain the deactivation and reactivation of the catalyst.

Key words: polymerization of ethylene over vanadium-magnesium catalysts, deactivation of catalyst in the presence of hydrogen, $Al(i\text{-}Bu)_3$ and $Al(i\text{-}Bu)_2H$ as cocatalysts, organoaluminum hydrides as deactivators.

In recent years, active research interest has been shown for supported catalysts for ethylene polymerization containing vanadium chlorides as active components [1—8]. As compared with well-known titanium-magnesium catalysts (TMC), these catalysts are promising for practical applications, because they exhibit some peculiarities and advantages allowing the molecular structure of polyethylene and ethylene copolymers with α-olefins to be controlled.

Unlike TMC, vanadium-magnesium catalysts (VMC) allow to produce polyethylene (PE) of a wide molecular weight distribution (*MWD*) [9, 10].

VMC are more capable of controlling PE molecular weight ($\overline{M}$) [6]. When ethylene is polymerized on TMC at 80°C, the PE molecular weight ranges from $1—2\cdot10^6$ (without hydrogen) to $2\cdot10^5$ (with $2.2\cdot10^{-2}$ mol/L of H_2). On VMC, under the same conditions, PE can be produced with molecular weights ranging from super high (over 10^7) to super low values ($4\cdot10^4$) [6]. The difference in the control of PE by TMC and VMC lies in the different sensitivities of these catalysts to hydrogen. Thus, the ratio between the rate constant for chain transfer from H_2 and the chain growth rate constant for VMC is essentially higher than that for TMC ($2.6\cdot10^5$ *vs.* $9.1\cdot10^3$) [6].

Supported VMC also exhibit a far higher copolymerizing ability than do TMC catalysts in the copolymerization of ethylene with various α-olefins. This effect continues to occur over a wide range of linear and branched olefins (Table 1) [11, 12]. Specially modified VMC allow to produce X-ray amorphous uniform ethylene copolymers with propylene possessing a rather narrow *MWD* [13].

Table 1. Data on comonomer reactivity ratio (r_1) in copolymerization of ethylene with α-olefins over Ti-Mg and V-Mg catalysts [12] [70°C; $Al(i\text{-}Bu)_3$]

α-Olefins	$TiCl_4/MgCl_2$	$VCl_4/MgCl_2$
Propene	13.0	3.8
1-Butene	28.6	12.7
1-Hexene	100	23
1-Octene	200	60
4-Methyl-1-pentene	140	31
3-Methyl-1-butene	500	132
3-Methyl-1-pentene	—	550
Norbornene	—	22

VMC synthesized by our method have shown a high and stable activity at 70—90°C without hydrogen and also with hydrogen present [1, 9, 10, 13].

Hydrogen is used to control the PE molecular weight with various types of polymerization catalysts. However, in the polymerization over vanadium-containing catalysts, hydrogen usually results in the decrease of catalyst activity [5, 14].

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In the present work we have studied the kinetics of ethylene polymerization over VMC in the presence of hydrogen to elucidate the factors causing deactivation of VMC.

EXPERIMENTAL

Catalysts were obtained by the procedure described elsewhere [10] by supporting vanadium tetrachloride and vanadium oxychloride ($VOCl_3$) on a highly dispersed magnesium dichloride. To synthesize the support, a solution of magnesium compound (composition $MgPh_2 \cdot 0.5\ MgCl_2$) in phenyl chloride mixed with dibutyl ether was chlorinated with CCl_4. The resulting catalyst contained 2.4 wt.% of vanadium, and exhibited a narrow particle size distribution, average particle size 30—40 µm.

Slurry polymerization of ethylene was performed in a steel 0.7 L reactor with intensive stirring. The standard conditions were as follows: heptane as solvent; polymerization temperature, 80—90°C; constant ethylene pressure; variable hydrogen pressure (H_2 was added at the beginning of polymerization); reaction time, 1 hour. Tri-isobutylaluminum (TIBA) was commonly used as a cocatalyst at concentrations of 2—10 mmols $Al(i\text{-}Bu)_3$/L. Standard TIBA concentration was 5 mmols/L. Di-isobutylaluminum hydride (DIBAH) was used as cocatalyst for comparison with TIBA in some experiments. Catalyst concentration was 0.04 g/L.

Polyethylene viscosity was determined in decalin at 408 K, and its molecular weight ($\overline{M}_v$) was calculated from the equation (1) [15]:

$$[\eta] = 2.55 \cdot 10^{-4} \cdot \overline{M}_v^{0.74} \qquad (1)$$

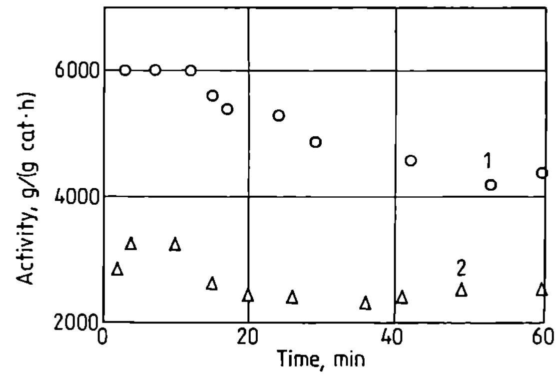


Fig. 1. The effect of hydrogen on ethylene polymerization over VMC; polymerization conditions: catalyst $VCl_4/MgCl_2$ (2.4% wt. V), heptane as solvent, 80°C, [TIBA] = 5 mmols/L, ethylene pressure 7.5 bar; 1 — without hydrogen, 2 — with hydrogen (0.5 bar)

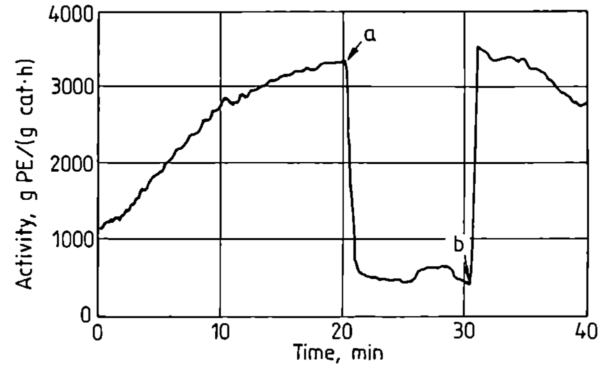


Fig. 2. The effect of hydrogen on ethylene polymerization over VMC; polymerization started with no hydrogen added, followed by: a) addition of H_2, b) degassing of H_2; polymerization conditions: catalyst $VCl_4/MgCl_2$ (1.7% wt. V), heptane as solvent, 80°C, [TIBA] = 7.6 mmols/L, ethylene pressure 2.44 bar, hydrogen pressure 0.25 bar

RESULTS AND DISCUSSION

Figure 1 shows the kinetic curves of ethylene slurry polymerization over VMC at 80°C with and without hydrogen. In each case the catalyst showed a fairly stable activity within 1 h operation.

Introduction of hydrogen into the ethylene polymerization slurry over VMC at the beginning (Fig. 1, curve 2) and in the middle of the run that had been started with no hydrogen added (Fig. 2a) caused a noticeable decrease in the catalyst activity. According to Fig. 2b, removal of hydrogen in the course of polymerization restored the starting activity of VMC. Therefore, deactivation of the catalyst by hydrogen is of reversible character. The same effect was shown earlier [5, 16].

Figure 3 shows how hydrogen concentration affects the VMC activity and PE molecular mass. Apparently, the introduction of hydrogen results in catalyst activity reduced by 6 times, as hydrogen concentration rises to 10 mmols H_2/L, which corresponds to a gas phase hydrogen concentration of 13 vol.%. A further increase in hydrogen concentration has no effect on the catalyst activity. The PE molecular weight is directly related to hydrogen concentration (Fig. 3).

The deactivation of the ($VCl_3 \cdot THF/SiO_2 + AlEt_2Cl$) catalyst by hydrogen in ethylene polymerization has been explained in terms of the effect of V-H bonds which may serve as sites for ethylene hydrogenation [14].

However, the chromatography analysis data obtained during ethylene polymerization on VMC in the presence of hydrogen show no ethylene hydrogenation to have occurred. Moreover, the catalyst activity is stable in time (Fig. 1) and does not depend on hydrogen concentration at $[H_2] > 10$ mmols/L at a simultaneous decrease of PE molecular weight (Fig. 3). Therefore, ethylene hydrogenation can not be the reason for VMC deactivation.

At a high concentration of hydrogen (20 mmols/L), when the catalyst activity does not depend on hydro-

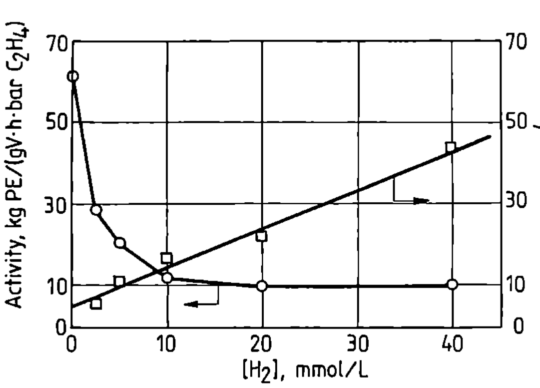


Fig. 3. The effect of hydrogen concentration on the activity of V-Mg catalyst and on $\overline{M}$ of polyethylene; polymerization conditions: catalyst $VOCl_3/MgCl_2$ (2.3% wt. V), 80°C, [TIBA] = 5 mmols/L, ethylene pressure 7.5 bar

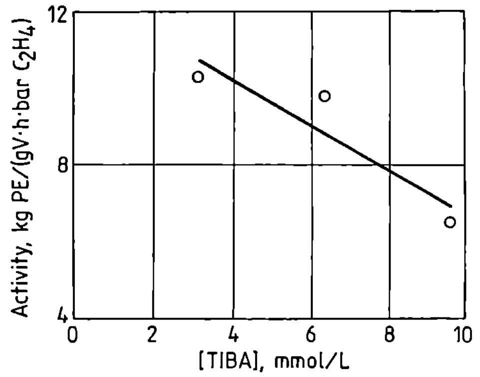


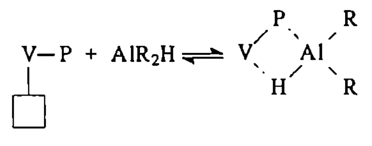
Fig. 4. The effect of TIBA concentration on the activity of the V-Mg catalyst (ethylene polymerization in the presence of hydrogen); polymerization conditions: catalyst $VCl_4/MgCl_2$ (2.4% wt. V), 80°C, ethylene pressure 7.5 bar, hydrogen pressure 2 bar ($[H_2]$ ~ 20 mmols/L)

gen concentration, we have studied the effect of cocatalyst concentration on the VMC activity (Fig. 4). Obviously, catalyst activity decreased, as TIBA concentration was increased. With no hydrogen added there is no well pronounced activity dependence on organoaluminum co-catalyst (OAC) concentration (Fig. 5, curve 1).

Therefore, in the presence of hydrogen the catalyst activity depends on the concentration of both hydrogen and OAC. Considering all the above data, we suggest the following routes of reactions to occur on VMC in the presence of hydrogen:

$$\text{V-P} + H_2 \rightarrow \text{V-H} + \text{polymer} \quad (2)$$

$$\text{V-H} + Al(i\text{-}C_4H_9)_3 \rightarrow \text{V-R} + Al(i\text{-}C_4H_9)_2H \quad (3)$$



$$\underset{\square}{\text{V}-\text{P}} + \text{AlR}_2\text{H} \rightleftharpoons \text{V}\begin{smallmatrix}\text{P}\\ \\ \text{H}\end{smallmatrix}\text{Al}\begin{smallmatrix}\text{R}\\ \\ \text{R}\end{smallmatrix} \quad (4)$$

$$R_2AlH \xrightleftharpoons{C_2H_4} R_2AlEt \quad (5)$$

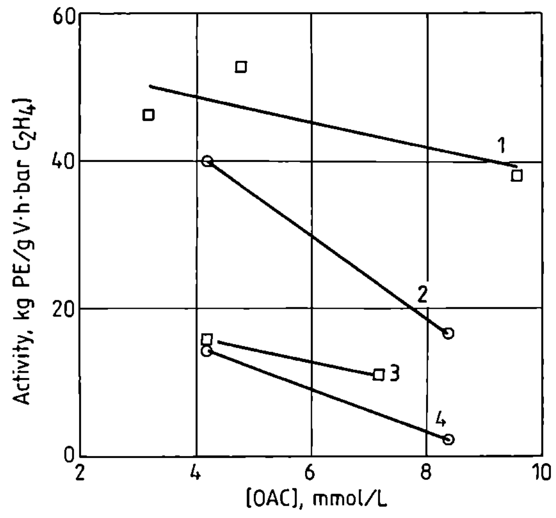


Fig. 5. DIBAH as cocatalyst, compared with TIBA: the effect of the cocatalyst concentration on the activity of V-Mg catalyst; polymerization conditions: catalyst $VCl_4/MgCl_2$ (2.4% wt. V), 80°C, ethylene pressure 3.5 bar, (without H_2) and 9 bar (with 0.5 bar H_2): 1 — cocatalyst TIBA (without H_2), 2 — cocatalyst DIBAH (without H_2), 3 — cocatalyst TIBA (with H_2), 4 — cocatalyst DIBAH (with H_2)

Polymer chain transfer from H_2 produces vanadium hydrides (reaction 2). We assume the surface vanadium hydrides to participate in the exchange with the cocatalyst (tri-alkyl aluminum) to yield monomer di-alkylaluminum hydride (reaction 3). This product is a strong complex generating agent, and is able to block active VMC sites *via* reaction 4. When hydrogen is removed from the reaction mixture, the catalyst is likely to be reactivated at the expense of the dialkylaluminum hydride conversion to trialkylaluminum by reaction (5).

A high concentration of vanadium hydrides, and thus of alkylaluminum hydride, is provided by a high rate constant of chain transfer with hydrogen over vanadium-magnesium catalysts [6].

In order to check our assumption that VMC is deactivated owing to the production of alkylaluminum hydrides, we studied ethylene polymerization on VMC in the presence of di-isobutylaluminum hydride (DIBAH) as cocatalyst.

However, the DIBAH forming *in situ* from vanadium hydrides, and the DIBAH introduced as cocatalyst, may differ in deactivating ability. Thus, the DIBAH produced in the reaction course may form as a highly active monomer directly participating in reaction (3), whereas the cocatalyst DIBAH stays as a less active associate [17]. Without hydrogen, di-isobutylaluminum hydride may interact with ethylene to yield tri-alkylaluminum [18].

Figure 5 shows how TIBA and DIBAH concentrations affect the activity of VMC. As DIBAH concentration increases, deactivation of the catalyst is indeed dramatic, especially in the polymerization with no hydrogen added (Fig. 5, curve 2). At high DIBAH concentrations,

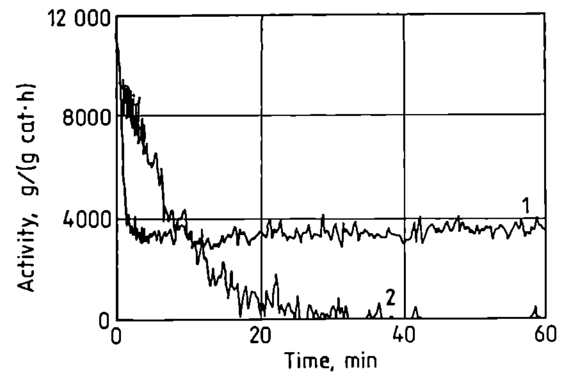


Fig. 6. The effect of DIBAH concentration on the activity of V-Mg catalyst in ethylene polymerization without H_2; polymerization conditions: catalyst $VCl_4/MgCl_2$ (2.4% wt. V), 80°C, ethylene pressure 3.5 bar: 1 — [DIBAH] = 4.2 mmols/L; 2 — [DIBAH] = 8.4 mmols/L

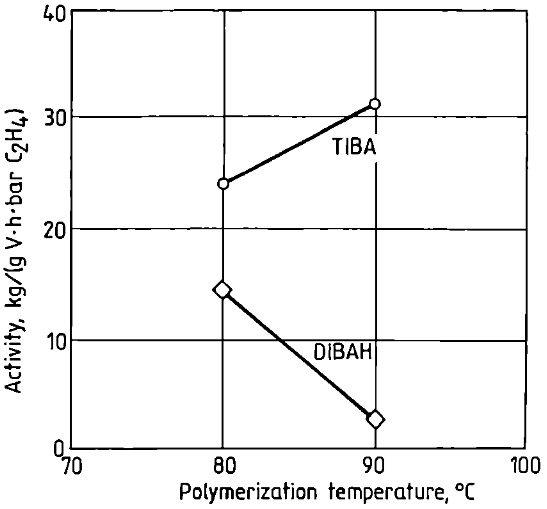


Fig. 7. DIBAH as cocatalyst, compared with TIBA; the effect of polymerization temperature on the activity of V-Mg catalyst; polymerization conditions: catalyst $VCl_4/MgCl_2$ (2.4% wt. V), 80°C, ethylene pressure 9.3 bar, hydrogen pressure 0.5 bar; [OAC] = 4—5 mmols/L

the catalyst is completely deactivated in 30 min (Fig. 6, curve 2).

The DIBAH co-catalyst has an identical dramatic effect on the VMC activity, when the polymerization temperature is increased. If, with TIBA, the polymerization temperature is increased from 80 to 90°C, the VMC activity improves, and with DIBAH the catalyst is quickly deactivated within the same temperature range (Fig. 7).

Therefore, alkylaluminum hydride, produced during ethylene polymerization over the VMC catalysts in the presence of hydrogen is, in all likelihood, the reason for catalyst deactivation. The hydride forms as the V-H bonds interact with AlR_3 followed by the adsorption of alkylaluminum hydride according to reactions 2—5.

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