Control of Product Selectivity by Catalyst Preparation in CO–H_2 Reactions over ZrO_2

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ZrO_2 catalysts prepared from $ZrO(NO_3)_2$ or $ZrOCl_2$ with NH_4OH or urea and calcined at 773 K showed selectivity for the formation of isobutene from CO and H_2, whereas catalysts prepared by hydrolysis of $Zr(OPr)_4$ or by calcination of ZrO_2 above 1573 K formed methane selectively.

It is well known that the method of preparation of catalysts can affect both activity and selectivity. We have found a clear relationship between selectivity and the catalyst preparation. The selective synthesis of isobutene from the CO–H_2 reaction over ZrO_2, reported previously,[1] has been found to change into selective methane formation by changing the catalyst preparation method, and we now report that in the CO–H_2 reaction over ZrO_2 the catalyst preparation controls the product selectivity.

Table 1 shows the product yield, the activity for hydrocarbon formation, and the surface area for various types of ZrO_2 catalyst. The activity for hydrocarbon yield was normalized

Table 1. CO–H_2 reaction over various ZrO_2 catalysts.[a]

Catalyst[b]	Reaction temp./K	Surface area/$m^2 g^{-1}$	Yield (μmol/1.5 g-cat.)[c] Hydrocarbon	MeOH+ MeOMe	CO_2	Activity[d]
ZrO_2 (N)[e]	623	53	39	12	238	0.020
ZrO_2 (Cl)[e]	623	52	30	7.5	168	0.016
ZrO_2 (C)[e]	623	6.8	6.1	6.0	36	0.024
ZrO_2 (N)[e]	673	53	83	0.14	350	0.040
ZrO_2 (U)[f]	673	36	98	3.2	335	0.075
ZrO_2 (1573)[f]	673	0.9	8.0	3.1	12	0.25
ZrO_2 (A)[f,g]	673	17	244	2.6	292	0.40

[a] Reactions were carried out in a gas-circulating glass vacuum system with an initial pressure of 0.68 atm (H_2/CO = 3) at a flow rate of about 40 ml (S.T.P.)/min. The catalysts (1.5 g) were evacuated at 973 K before reaction. [b] ZrO_2 (N) and ZrO_2 (Cl) were prepared with NH_4OH from $ZrO(NO_3)_2$ and $ZrOCl_2$, respectively. ZrO_2 (C) was obtained from Kanto Chemicals Inc. ZrO_2 (U) was prepared from $ZrO(NO_3)_2$ with urea. ZrO_2 (1573) was obtained by calcination of ZrO_2 (N) at 1573 K for 3 h. ZrO_2 (A) was prepared by the hydrolysis of $Zr(OPr)_4$. [c] Products were collected at liquid nitrogen temperature except for methane and analysed by g.c., mass spectral, and i.r. methods. [d] μmol of hydrocarbons m^{-2} h^{-1}. [e] Products were collected for the initial 25 h. [f] Products were collected for the initial 24 h. [g] Initial pressure 0.85 atm, flow rate ~660 ml (S.T.P.)/min.

with respect to surface area. The product distribution for hydrocarbons is shown in Figure 1. There are two types of distribution. One, shown by ZrO_2 (C), ZrO_2 (1573), and ZrO_2 (A) catalysts, has high selectivity for methane formation, the selectivity being the highest (94 mol%) over ZrO_2 (A). On the other hand, ZrO_2 (N), ZrO_2 (Cl), and ZrO_2 (U) catalysts show high selectivity for C_4 hydrocarbon formation, the selectivity for methane formation being <15 mol% and that for C_4 hydrocarbons being >75 mol% at 623 K and 60% at 673 K. The activities shown in Table 1 seem to indicate that the rates of hydrocarbon formation with methanation catalysts are much higher than with those favouring C_4 hydrocarbon formation. However, the differences are rather small if the rates are evaluated on the basis of carbon atoms formed as hydrocarbons. The change in product selectivity is brought about only by changes in catalyst preparation method and the activity differences between the catalysts are rather small.

X-Ray diffraction patterns of ZrO_2 (A) and ZrO_2 (C) showed small peaks due to the tetragonal phase in addition to large peaks due to the monoclinic phase, whereas the presence of the tetragonal phase was not detected for the other four oxides.† Thus, there seems to be no direct relation between the selectivity and the crystal structure.

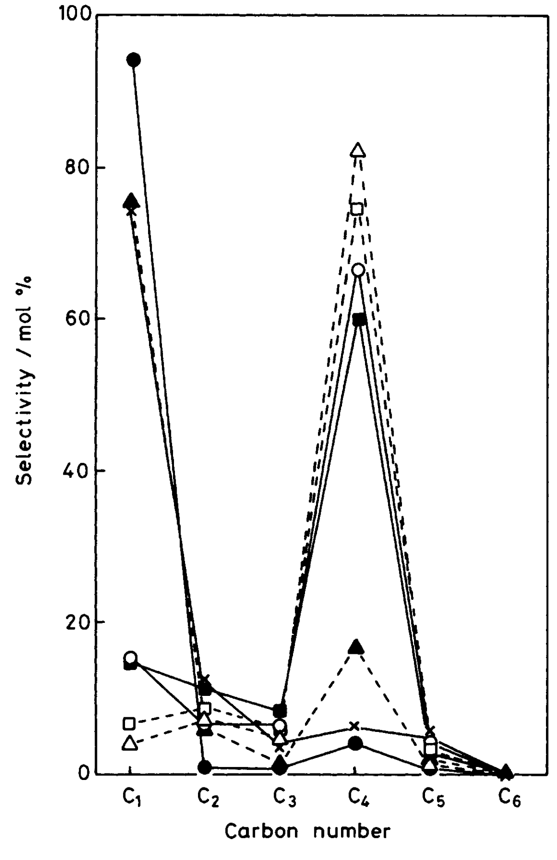

Figure 1. Hydrocarbon product distributions for various ZrO_2 catalysts. △: ZrO_2(N) (623 K), □: ZrO_2(Cl) (623 K), ▲: ZrO_2(C) (623 K), ○: ZrO_2(N) (673 K), ■: ZrO_2(U) (673 K), ×: ZrO_2 (1573) (673 K), and, ●: ZrO_2(A) (673 K), the reaction temperatures being shown in parentheses.

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References

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† It is known that zirconium oxide calcined above about 1373 K has a tetragonal structure which slowly changes into the monoclinic form at lower temperatures (ref. 2). The absence of the tetragonal phase in ZrO_2 (1573) may be due to the slow cooling in an oven after the calcination.