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NEW "Pd / ULTRA-THIN AMORPHOUS-OXIDE LAYER /ZSM-5" CATALYSTS FOR SELECTIVE FORMATION OF PROPANE FROM CO/H_2

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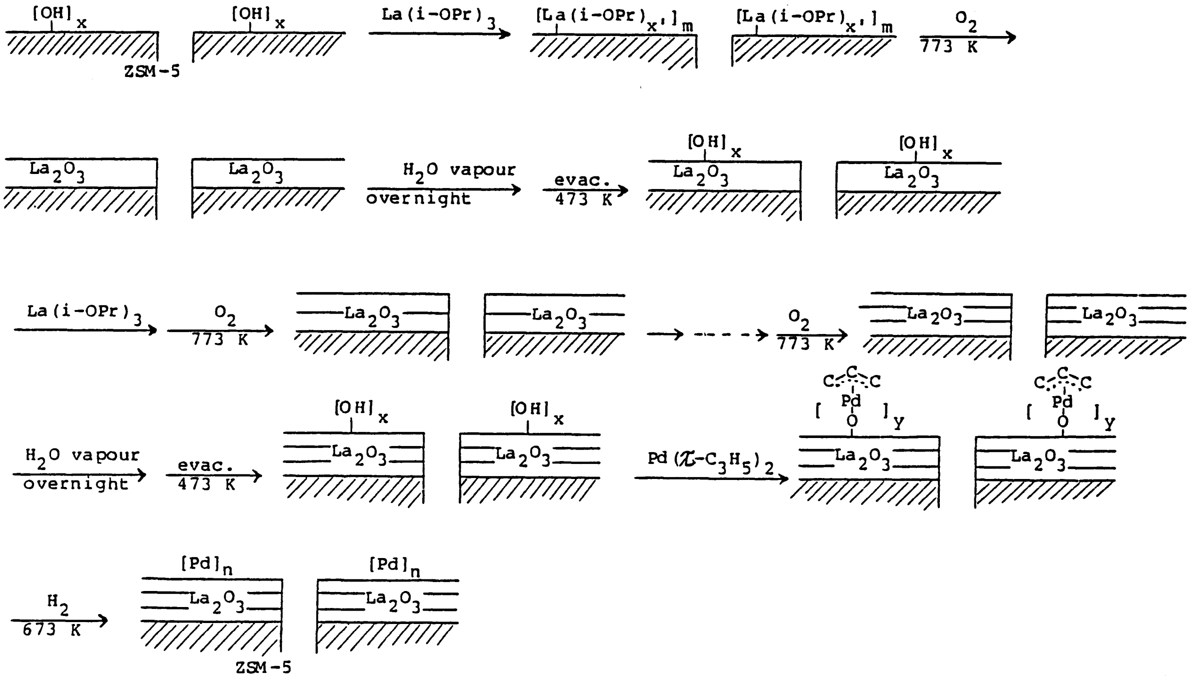
Among new three types of "Pd / ultra-thin amorphous-oxide(La_2O_3, SiO_2, or TiO_2) layers / ZSM-5" catalysts, prepared by a two-stage attaching technique, the La_2O_3-coated ZSM-5 -supported Pd catalyst was found to be a selective catalyst for propane formation (68%) from CO and H_2 at 543 K and 1.01 MPa.

It is still acutely difficult to convert carbon monoxide to a particular hydrocarbon with a good selectivity; exceptional metal catalysts are Co-Cd/A-zeolite,[1)] $FeCl_3$/graphite-Na/naphthalene,[2)] Cr_2O_3/ZnO-ZSM-5,[3)] and Mo-monomer/SiO_2[4)] for the formations of propene (≈100%), acetylene (93%), ethane (85%), and ethane (70%), respectively, the products being C_2 hydrocarbons except for propene. We report the selective catalysis of new "Pd/three-monolayer amorphous metal-oxide/ZSM-5" catalysts for propane formation from CO and H_2.

Catalysts were prepared by a two-stage attaching technique. At first, hydroxyl groups of the external surface (14 m^2g^{-1}) of a 473 K- pretreated ZSM-5 (H-type, $SiO_2/Al_2O_3=81.7$)[5)] were interacted with lanthanum isopropoxide ($La(i\text{-}OPr)_3/OH=3$) in a reflux hexane (Na-wire-dried) under atmospheric pressure of Ar (99.9995%), followed by decantation to remove a residual $La(i\text{-}OPr)_3$ and then by oxidation at 773 K. The lanthana layer attached to the external surface of ZSM-5 was exposed to water vapour overnight to form new OH groups on the lanthana layer. The sample was treated at 473 K under vacuum and the reaction with $La(i\text{-}OPr)_3$ was repeated again. Finally, three atomic layers of La_2O_3 were attached onto ZSM-5 external surfaces. Subsequently palladium was supported on the La_2O_3 layers by the reaction between hydroxyls of the La_2O_3 surface and $Pd(\pi\text{-}C_3H_5)_2$; a C_3H_5 ligand reacted with an OH group. The attached Pd species were reduced with H_2 at 673 K to lead to the formation of Pd metal particles supported on the ultra-thin layers of lanthana. These steps for the preparation of $Pd/La_2O_3/ZSM$-5 are illustrated in Scheme 1. $Pd/SiO_2/ZSM$-5 and $Pd/TiO_2/ZSM$-5 were prepared in almost the same way, but in these samples methyltriethoxysilane ($CH_3Si(OEt)_3$) or titanium isopropoxide ($Ti(i\text{-}OPr)_4$) vapour was contacted with the hydroxyls of ZSM-5 surfaces at 473 K under vacuum. The alkoxides of La, Si, and Ti with large molecular size were chosen not to enter the cavities of zeolite. The Pd-loadings (wt% in catalysts) were 0.94% (La_2O_3), 0.95% (SiO_2), and 0.42% (TiO_2).



Scheme 1. Illustration of the preparation of "Pd/three-atomic La_2O_3-layers/ZSM-5" catalyst.

The intensity profiles of X-ray microanalysis (XMA) and the high resolution TEM images of the samples coated with three atomic oxide-layers which was indicated by gravimetric and X-ray fluorescence (XRF) analyses suggested the layer-like-coated surfaces with nearly constant thickness, island-like oxides on ZSM-5 substrate being never observed. The X-ray diffration (XRD) and electron diffraction (ED) showed neither peak nor pattern for crystalline La_2O_3, SiO_2, or TiO_2, while for a mixture of these metal oxides and ZSM-5 with the same composition sharp XRD peaks of the metal oxide were observed. These results together with the fact that the lattice constants of La_2O_3 and TiO_2 are incoherent with that of ZSM-5 indicate that the aultra-thin oxide layers are amorphous. The pore diameters of ZSM-5 remained

Table 1. Syn-gas conversion on zeolite-based, doubly-attached and physically-mixed catalysts[a)]

Catalysts[b)]	Temp/K	Conv./%[c)]	Selec./%			Distributions of Hydrocarbons / %[f)]						
			H.C.[d)]	Oxy.[e)]	CO_2	C_1	C_2^-	$C_2^=$	C_3^-	$C_3^=$	C_4	C_5^+ [g)]
$Pd/La_2O_3/Z$	473	0.6	60.9	39.1	0.0	84.9	6.4	5.9	1.6	1.6	0.0	0.0
	543	1.6	89.2	9.0	1.8	3.0	2.2	0.1	68.4	2.6	9.0	14.7
	573	2.0	96.0	0.6	3.4	15.1	9.3	0.5	48.4	2.0	9.1	15.6
	623	4.9	94.0	0.2	5.8	34.2	8.7	0.7	33.0	1.4	8.3	13.7
$(Pd/La_2O_3)+Z$	543	0.3	100	0.0	0.0	51.7	15.4	3.5	5.9	7.8	9.5	6.3
$Pd/SiO_2/Z$	473	0.15	99.9	0.1	0.0	89.0	4.9	2.5	1.1	1.1	1.4	0.0
	543	0.3	96.6	3.4	0.0	15.5	33.5	0.4	44.0	1.9	4.7	0.0
	573	0.4	99.2	0.8	0.0	19.5	21.7	0.5	45.5	1.8	6.8	4.2
	623	1.0	99.6	0.4	0.0	28.8	10.8	1.3	42.9	2.4	8.2	5.6
$(Pd/SiO_2)+Z$	543	0.04	100	0.0	0.0	69.0	8.9	4.4	7.5	7.5	2.7	0.0
$Pd/TiO_2/Z$	473	0.4	100	0.0	0.0	87.2	9.6	3.2	0.0	0.0	0.0	0.0
	543	0.6	99.2	0.8	0.0	21.5	30.3	0.3	34.2	1.3	6.3	6.1
	573	0.8	99.8	0.2	0.0	32.0	29.4	0.4	26.4	1.3	5.1	5.4
	623	1.8	94.3	0.3	5.4	57.6	17.1	0.4	18.3	0.9	3.2	2.5
$(Pd/TiO_2)+Z$	543	0.1	100	0.0	0.0	75.0	10.2	1.9	5.6	4.6	2.7	0.0

a) Catalyst=1 g, P=1.01 MPa, $CO/H_2=1/2$, SV=3600 h^{-1}(1.01 MPa, 300 K). The data were taken during the first hour of run. The conversion decreased gradually with time; for example, for $Pd/La_2O_3/Z$ catalyst, to 43 % level of the initial conversion after 13 h on stream at 543 K. b) Z: ZSM-5. c) Conversion(%) is defined as: $100\times\Sigma$(products)/(CO)-input on C-base. d) C_1-C_7 hydrocarbons. e) $CH_3OH + CH_3OCH_3$.
f) C_n^-: alkanes, $C_n^=$: alkenes. The selectivity(71%) to C_3 declined slowly to 65% after 13 h on stream.
g) C_5-C_7 H.C. were produced.

unchanged by the attachment of the three-atomic amorphous layers.

The particle sizes of Pd on these oxide/ZSM-5 were 60 Å on average (H/Pd and TEM), the size being suitable for methanol formation.$^{6,7)}$

CO hydrogenation was studied in a pressurized flow-type reactor (0.10-1.01 MPa) equipped with two double-column-type gas-chromatographs (TCD & FID) for product analyses. In CO hydrogenation at atmospheric pressure (CO/H_2=1/2) and T=473-723 K, the palladium supported on the ultra-thin amorphous-oxide layer-coated ZSM-5 showed little activity for methanol formation and methane was predominantly formed. Methanol formation on the Pd/La_2O_3/ZSM-5 catalyst at 473 K markedly increased with an increase of the pressure to 1.01 MPa. The catalyst was much more active than a physical mixture of a usual La_2O_3-supported Pd catalyst and ZSM-5 for methanol synthesis.

The yields of C_2^+-hydrocarbons increased drastically at temperatures above 543 K as shown in Table 1. It is to be noted that 71% of total hydrocarbons formed in CO hydrogenation on Pd/La_2O_3/ZSM-5 at 543 K were C_3 components, more than 96% of which being propane. In addition, C_2- and C_4-yields were as few as 2.3% and 9.0%, respectively. The Pd/SiO_2/ZSM-5 catalyst was less active as compared with the Pd/La_2O_3/ZSM-5 catalyst, but the C_2 population was relatively high, resulting in 80% selectivity to C_2 and C_3 hydrocarbons at 543 K. On the Pd/TiO_2/ZSM-5 catalyst a specific feature in product distributions was not observed.

The reason that the "Pd / ultra-thin amorphous-oxide layer / ZSM-5" catalysts showed specific product ditributions, particularly propane being selectively formed on Pd/La_2O_3/ZSM-5, is not so clear at the present, but usual mixed catalysts, (Pd/La_2O_3)+(ZSM-5), (Pd/SiO_2)+(ZSM-5) and (Pd/TiO_2)+(ZSM-5), were much less active and not selective as shown in Table 1. The samples of Pd supported on "ultra-thin layers of amorphous oxides attached to ZSM-5 external surfaces provide a new class of catalysts.

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