Effect of Sodium Cation Addition on the Hydroformylation of Propene over Silica-supported Group VIII Metal Catalysts

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Addition of a sodium cation to silica-supported Rh, Pd, Pt, and Ni catalysts markedly lowers the activation energy of the hydroformylation process without affecting the regioselectivity of the products and facilitates the CO insertion into propyl intermediates.

Hydroformylation of alkenes by heterogeneous catalysts are less extensively studied[1—3] than by homogeneous transition metal complexes.[4—6] Recently some metal cations such as Zn, Ti, and Fe were demonstrated to show promotion effect upon the hydroformylation of ethene over Rh/SiO_2.[7] As yet, no investigations have been reported on the promotion effect of alkali metals on the hydroformylation reaction. In this Communication we report the effect of an added sodium cation on the hydroformylation of propene over silica-supported Rh, Pd, Pt, and Ni catalysts, which is studied by applying an isotope tracer technique involving microwave spectroscopy.[8]

Catalysts (5 wt%) were prepared by impregnating aqueous solutions of the corresponding metal chlorides ($RhCl_3$, $PdCl_2$, H_2PtCl_6, and $NiCl_2$) onto SiO_2 (Aerosil 300, Nippon Aerosil, 300 m^2/g). The sodium cation was added in the form of NaCl with the molar ratio of 2(NaCl) : 1($PdCl_2$, H_2PtCl_6, or $NiCl_2$) and 3(NaCl) : 1($RhCl_3$). The catalyst (0.2 g) was put in a U-shaped glass reactor, which was connected to a closed gas circulation system, and was reduced by hydrogen at 723 K for several hours. The dispersion of the metals was determined by CO chemisorption at room temperature, assuming the stoicheiometry of CO : M = 1 : 1. The reaction was carried out in the same closed gas circulation system. A dry-ice–acetone cold trap was used to gather the aldehydes and alcohols formed during the reaction. The products were analysed by g.c., and their deuterium content was determined by m.s. The location of the deuterium atom in monodeuteriopropene was determined by microwave spectroscopy.

When a mixture of C_3H_6 (3.3 kPa), CO (6.7 kPa), and H_2 (13.3 kPa) was introduced on these catalysts at the temperature of 300 to 450 K, hydrogenation and hydroformylation of propene simultaneously took place, and propane, n- and s-butyraldehyde and n- and s-butyl alcohol were formed. Turnover frequency (TOF) (reaction rate per surface metal atom) and activation energy (AE) of these processes as well as regioselectivity of hydroformylation process are summarized in Table 1. Activity and selectivity depended on the kind of metal catalysts employed. In the case of Rh catalyst (388 K), the rate of propane formation increased drastically by the addition of the sodium cation. However, because of the simultaneous decrease in activation energy of this process (from 97 to 78 kJ/mol), the promotion effect was small at higher temperatures. A similar situation was observed for hydroformylation over Rh, Pd, and Pt catalysts. The added sodium cation accelerates the hydroformylation by 2 to 3 times and at the same time decreases the activation energy by 20 kJ/mol. The regioselectivity of the hydroformylation process was also markedly dependent on the metals employed. It is worth noting that addition of the sodium cation did not affect the regioselectivity at all, as shown in Table 1.

To investigate this situation further, a C_3H_6–CO–D_2 reaction was carried out over these catalysts. Deuterium exchange reaction of propene proceeded more than 1 order of magnitude faster than the hydrogenation and hydroformylation processes. Isotopic distribution of formed monodeuteriopropene was analysed by microwave spectroscopy. With this technique it is possible to estimate the ratio of n-propyl to

Table 1. Hydrogenation and hydroformylation of propene over various catalysts

Catalysts	Reaction T/K	Dispersion	TOF/$\times 10^{-6}$ sec^{-1}		AE/kJ mol^{-1}		Selectivity/%			
			Propane	HF[a]	Propane	HF[a]	n-Ald.[b]	s-Ald.[b]	n-Alc.[c]	s-Alc.[c]
Rh	388	0.52	3.8	2.1	97	57	51	15	23	11
Rh–Na	388	0.40	30	9.4	78	33	52	15	22	11
Pd	300	0.08	130	2.2	75	69	14	48	8	30
Pd–Na	300	0.13	49	5.4	74	36	23	43	8	26
Pt	453	0.36	510	15	105	60	21	18	32	29
Pt–Na	453	0.21	210	25	97	42	21	18	31	30
Ni	453	0.41	330	1.5	—	—	9	2	79	10
Ni–Na	453	0.26	120	2.1	—	—	8	2	81	9

[a] HF = hydroformylation. [b] Ald = aldehyde. [c] Alc = alcohol.

s-propyl adsorbed species, because $H_2C=CD-CH_3$ can be formed through the n-propyl intermediate and $HDC=CH-CH_3$ + $H_2C=CH-CH_2D$ through the s-propyl intermediate. The isotopic distribution patterns obtained indicate the ratio of n-propyl to s-propyl adsorbed species to be as follows; Rh(60 : 40), Pd(10 : 90), Pt(50 : 50), and Ni(90 : 10). These ratios correspond surprisingly well to those of the regioselectivities mentioned above, suggesting that both processes proceed through similar reaction intermediates. Addition of the sodium cation did not affect them at all as in the case of hydroformylation. Isotope effects on these processes were examined by comparing the initial rates in C_3H_6–CO–H_2 (k_H) and C_3D_6–CO–D_2 (k_D) reactions. For propane formation, a normal isotope effect (k_H/k_D = 1.2—1.5) was observed, whereas an inverse isotope effect (k_H/k_D = 0.9—0.7) was observed during hydroformylation.

From these experimental results we propose the following reaction mechanism. A rapid equilibrium exists between the adsorbed propene and propyl intermediates, and the added sodium cation does not affect this step at all. The rate determining step in the propane formation is that of the second hydrogen addition. The inversion isotope effect in hydroformylation strongly suggests that the rate determining step in this process is the CO insertion into the adsorbed propyl species. The sodium cation lowers the activation energy of this process by forming some surface sites favourable to CO insertion and also by stabilizing the acyl intermediates.

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