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Stereochemistry on the Catalytic Hydrogenation of 1-*t*-Butyl-4-methylenecyclohexane over Modified Raney Ni, Co, and Fe Catalysts

Shin Imaizumi,* Hitoshi Murayama, Jun-ichi Ishiyama, and Yasuhisa Senda
Department of Engineering Science (Chemistry), Faculty of Engineering, Tohoku University,
Aoba, Sendai 980

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Synopsis. Contrary to a fresh catalyst, aged Raney Ni in ethanol provided exclusively a less stable product in the hydrogenation of the title compound. A similar stereoselectivity was observed over a catalyst which was refluxed in ethanol as well as that treated with carbon monoxide. These results indicate that the catalyst stored in ethanol is modified with carbon monoxide generated by the decomposition of the solvent.

Mitsui and his coworkers found that the Raney Ni catalyst stored in ethanol shows; i) a different stereoselectivity to Pt, Rh, and Pd catalysts in the hydrogenation of alkylmethylenecyclohexanes[1] and alkylmethylcyclohexenes,[2] ii) the appreciable anchor effect of a hydroxyl group in the hydrogenation of substituted cyclohexanols.[3] They suggested that the product-controlling step of the hydrogenation over Raney Ni is the adsorption of the substrate on the catalyst.[1–3] Tyman reported that the hydrogenation of 1-methyl-3- and 4-methylenecyclohexane over Raney Ni aged in methanol preferably gave the thermodynamically less stable of two possible products, while alternatives were obtained over a new catalyst.[4]

In order to examine the characteristics of the Raney Ni catalyst aged in ethanol, 1-*t*-butyl-4-methylenecyclohexane (**1**) and 4-*t*-butyl-1-methylcyclohexene (**3**) were hydrogenated under various selected conditions.

Results and Discussion

The stereoselectivity on the hydrogenation of **1** over Raney Ni varied appreciably depending on the origin of the catalysts and the reaction conditions (Tables 1 and 2). A thermodynamically more stable product, *trans*-1-*t*-butyl-4-methylcyclohexane (**2e**), was predominantly obtained over fresh Raney Ni. The amount of **2e** decreased in an atmosphere of hydrogen, and increased with the amount of the catalyst. This suggests that the amount of hydrogen available on the catalyst surface is also responsible for the stereochemistry on the hydrogenation of a reactive substrate such as **1**.[5,6] When Raney Ni which had been stored in ethanol for 40 d was used, a thermodynamically less-stable product, *cis*-1-*t*-butyl-4-methylcyclohexane (**2a**), was selectively yielded regardless of the amount of the catalyst and pressure of the hydrogen. Contrary to this, the stereoselectivity over a catalyst aged in water or cyclohexane was not as high as that over a catalyst aged in ethanol (Table 1).

The proportion of products over a catalyst modified under various conditions are shown in Table 2. The catalyst refluxed in methanol and ethanol under a nitrogen atmosphere showed a similar stereoselectivity to that aged in ethanol, while **2e** was still predominant over the catalyst refluxed in 2-propanol, 2-methyl-2-propanol, tetrahydrofuran or cyclohexane. The catalyst which was stirred in ethanol or cyclohexane under an atmosphere at room temperature for 2 h showed a stereoselectivity analogous to the aged catalyst in the respective solvent for 40 d. Moreover, **2a** was selectively formed over a fresh catalyst which was treated with carbon monoxide in cyclohexane as well as in ethanol. It has been shown that ethanol is decomposed to carbon monoxide and methane by refluxing over Raney Ni.[7] Consequently, it is clear that the high selectivity of the axial methyl product on use of the catalyst stored in ethanol is attributed to

Table 1. Effect of storage on the stereoselectivity in the hydrogenation of 1-*t*-butyl-4-methylenecyclohexane (**1**)[a]

Catalyst	Weight[b] (mg)	H_2 (kg/cm^2)	Solvent	Initial	Products (a-Me %)[c] Period of storage (days)			
					10	20	30	40
Raney Ni	30	1	EtOH	46 (7)[d]	56 (7)	69 (3)	81 (3)	94 (1)
	100	1	EtOH	35 (7)	44 (8)	60 (6)	84 (3)	93 (2)
	500	1	EtOH	23 (11)	27 (13)	43 (8)	87 (3)	95 (1)
	500	25	EtOH	42 (4)				
	500	100	EtOH	47 (3)	57 (5)	71 (6)	80 (3)	96 (1)
	500	1	H_2O	23 (13)		27 (13)		46 (8)
	500	1	C_6H_{12}[e]	14 (14)		46 (8)		63 (5)
Raney Co	50	1	EtOH	33 (0)		35 (0)		39 (0)
	500	1	EtOH	29 (0)		30 (0)		39 (0)
	500	100	EtOH	46 (0)				
Raney Fe	50	1	EtOH	55 (2)	72 (2)			
	500	1	EtOH	35 (5)	50 (5)	54 (5)	71 (4)	
	500	100	EtOH	58 (2)	69 (2)	75 (2)	80 (2)	

a) Substrate; 0.5 mmol, Solvent; Ethanol 5 ml, Ambient temperature. b) Weight of wet state containing about 40% of solvent. c) a-Me% = **2a**/**2a** + **2e** × 100. d) Is% = **3**/**2a** + **2e** + **3** × 100, given in parentheses. e) Cyclohexane 5 ml.

Table 2. Effect of modification of fresh catalyst on the stereoselectivty in the hydrogenation of 1-*t*-butyl-4-methylenecyclohexane (**1**)[a]

Catalyst	Solvent	Untreated	Products (a-Me %)[b] Modification			
			Reflux[c]	Air[d]	CO[e]	*n*-BuNH$_2$[f]
Raney Ni	MeOH	20 (13)[g]	87 (3)			
	EtOH	23 (11)	94 (1)	96 (1)	98 (1)	49 (0)
	2-PrOH	16 (14)	23 (14)			
	2-Me-2-PrOH	15 (15)	27 (34)			
	THF	12 (14)	26 (11)			
	C_6H_{12}	14 (14)	24 (47)	60 (4)	88 (2)	60 (0)
Raney Co	EtOH	29 (0)	32 (0)	48 (0)	51 (0)	17 (0)
	C_6H_{12}	29 (0)	35 (0)	40 (0)	44 (0)	14 (0)
Raney Fe	EtOH	35 (5)	83 (3)	53 (5)	80 (3)	38 (0)
	C_6H_{12}	32 (8)	41 (8)	53 (5)	84 (3)	39 (0)

a) Substrate; 0.5 mmol, Catalyst; 0.5 g (wet), Solvent; 5 ml, Ambient temperature and pressure. b) See Table 1, footnote c. c) Refluxed in given solvent for 2 h under N_2 atmosphere. d) Stirred gently in given solvent for 2 h at ambient temperature under air. e) Introduced 100 μmol of CO, then stirred for 0.5 h at ambient temperature under hydrogen atmosphere. f) Added 100 μmol of *n*-BuNH$_2$, then stirred for 0.5 h at ambient temperature under hydrogen atmosphere. g) See Table 1, footnote d.

carbon monoxide formed from ethanol rather than the partial oxidation of the catalyst.

The hydrogenation of **1** over Raney Ni aged in ethanol for a long time gave exclusively **2a** irrespective of the hydrogen pressure and the amount of catalyst. This indicates the following: i) The interaction between the catalyst and the substrate plays a major role in determining the product distribution, ii) the hydrogen available on a catalyst surface does not directly contribute to the determination of the product distribution. These results indicate that the product-controlling step is the adsorption of the substrate on the catalyst in the hydrogenation over Raney Ni which is poisoned by carbon monoxide. On the other hand, the product-controlling step is not primarily defined to be the adsorption of the substrate on fresh Raney Ni.

3, which is generated by the double-bond migration of **1** during the hydrogenation, was also hydrogenated. No appreciable stereoselectivity was observed and the apparent rate of reaction was very slow compared to that of **1**. This means that the stereoselectivity which appears in Tables 1 and 2 is primarily the results from the direct hydrogenation of **1**.

The thermodynamically more stable product (**2e**) was preferred in the hydrogenation of **1** over fresh Raney Co. No effect of a storing period as well as refluxing under a nitrogen atmosphere was observed on the product ratio. The effects of air and carbon monoxide on Raney Co were not appreciable compared to those on Raney Ni. When the catalysts were treated with *n*-BuNH$_2$, the amount of **2a** increased over Raney Ni compared to that over the parent catalyst, while more than 80% of **2e** was yielded over Raney Co (Table 2). No endocyclic olefin which was derived from the starting material by the double bond migration was detected in the hydrogenation (Tables 1 and 2). Such differences in the effects regarding the modification of Raney Ni and Raney Co give important information to elucidate the characteristics of both Ni and Co catalysts.

Experimental

Catalyst. Raney Ni was prepared from Raney Ni NDH (Kawaken Fine Chemicals Co.) by the W-4 method.[8] The catalyst was stored at room temperature. Raney Co and Fe were prepared from Raney Co OD and Fe ND (Kawaken Fine Chemicals Co.) by an analogous method as Raney Ni.

Catalytic Hydrogenation. 0.5 mmol of substrate and a known amount of catalyst (contains *ca.* 40 wt% of solvent) in a solvent (5 ml) were stirred with hydrogen at an atmospheric or a high pressure and room temperature. The reaction was followed gas chromatographically by analyzing aliquots of the reaction mixture at appropriate time intervals.

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