Selective Synthesis of Alk-1-enes from CO/H_2 Catalysed by Highly Reduced Zeolite-entrapped Cobalt Clusters

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Highly reduced zeolite-entrapped cobalt particles are prepared by simple impregnation of an alkali solution into a cobalt-exchanged zeolite followed by reduction with hydrogen gas at 450 °C; the catalyst exhibits high selectivity towards linear hydrocarbons, especially alk-1-enes, and strong resistance to deactivation in the Fischer–Tropsch reaction.

Attempts have been made to encapsulate metal clusters within molecular-sized cages of zeolite for possible control of product selectivity in the Fischer–Tropsch reaction. One way to achieve this goal is to reduce ion-exchanged metal cations inside zeolite pores with hydrogen gas. For iron or cobalt, however, this procedure has not been successful. Ion-exchanged iron cations in zeolite were not reduced to metal,[1] and ion-exchanged cobalt cations were reduced to a very low degree (less than 5% after hydrogen reduction at 500 °C).[2] Fraenkel and Gates[3] used cadmium vapour to reduce cobalt-exchanged zeolites and some of these showed very high selectivity towards propylene or n-butane. Activity was, however, decreased gradually at reaction temperatures higher than 180 °C. Another preparation technique is introduction of volatile organometallic compounds having zero-valent cobalt into zeolite pores and subsequent decomposition in an air-free environment, as illustrated by Ozin *et al.*[4] The method yielded low metal loading (less than 1%), however, and CO hydrogenation reaction over the catalyst showed that an appreciable portion of alkenes were branched isomers although the alkene selectivity was very high. McMahon *et al.*[5] used a microwave discharge technique to decompose cobalt carbonyl (0.8% of Co) impregnated in the zeolite cage. Highly dispersed small cobalt clusters were formed inside the zeolite cage, but there was no mention of the formation of hydrocarbon isomers although a high selectivity toward alkenes (alkene: alkane = 1.2 ~ 1.5 : 1) was claimed in the hydrocarbon range of C_1–C_{10}.

During the study of iron-loaded mordenites,[6] we have found that injection of a high concentration (3 mol dm^{-3}) of NaOH solution into the pores of iron-exchanged zeolite could promote reduction of iron cations in the zeolite; *ca.* 27% of iron was found to be reduced after heating in hydrogen gas at 450 °C. It was thought that the injected sodium ions would exchange with the iron cations in iron-exchanged zeolite, and that the iron cations detached from the zeolite framework could be easily reduced with hydrogen. In the present study, the method was applied to cobalt-exchanged zeolite, which is easier to reduce than iron-exchanged zeolite. It was found that cobalt-exchanged zeolite X was very successfully reduced (78%), and the catalyst exhibited high selectivity towards straight chain hydrocarbons, especially toward alk-1-enes during the synthesis reaction.

The catalyst was prepared as follows: the cobalt ions were loaded onto zeolite X by the ion-exchange method (hereafter abbreviated as CoX). The cobalt loading was found to be 7.2 wt% on the basis of dry zeolite. Injection of alkali solution into the pores of the zeolite was performed as follows. The zeolite was first dehydrated by heating it in air at 400 °C for 3 h. After cooling to room temperature, the sample was impregnated with 5 mol dm^{-3} aqueous solution of NaOH to the point of incipient wetness. The sodium-injected slurry was immediately filtered and washed with 1 mol dm^{-3} NaOH solution and then dried at 120 °C (abbreviated as CoX-Na). The washing step was intended to remove any cobalt deposit left on the exterior surface of zeolite crystal and to neutralize the acidic sites on zeolite. An impregnated catalyst (abbreviated as Co/X) with cobalt loading 6.1 wt% was also prepared by the incipient-wetness method. All the catalysts were reduced with hydrogen gas at 450 °C for 8 h prior to the experiments.

Data for the steady-state activity tests in the Fischer–Tropsch reaction (CO/H_2 mol ratio, 1.0) are shown in Table 1. As expected, the ion-exchanged CoX was reduced negligibly and catalytic activity was very low. However, the sodium-treated CoX-Na showed a remarkable enhancement of reduction, as high as that of the impregnated catalyst, Co/X. Average particle size of reduced cobalt in the impregnated

Table 1 Degree of reduction and product distribution over various catalysts

Catalyst	% Co[a] reduced	T/°C	Pressure /atm	Conversion (%)	Selectivity (%)[b]				% CO_2[c]	Average carbon number[d]
					C_1	alk-1-ene	n-alkane	isomer		
CoX	tr.	250	1	0.04	60.7	26.5	3.5	9.5	16.4	1.8
		260	1	0.08	68.4	20.6	4.7	6.3	17.4	1.6
		270	1	0.14	74.9	15.5	5.4	4.1	15.8	1.5
Co/X	71.6	240	1	0.71	28.2	33.5	6.7	31.6		3.7
		260	1	1.63	38.2	27.3	7.5	27.0		3.0
		280	1	2.83	57.0	20.2	7.0	16.8		2.1
CoX-Na	78.6	230	1	0.53	11.1	60.8	18.5	9.7	29.3	7.8
		240	1	1.09	11.1	59.2	16.1	13.3	26.5	7.3
		260	1	2.38	12.1	53.4	19.5	15.0	22.8	6.2
		230	10	1.87	18.9	43.4	23.0	14.7		5.7
		230	30	1.91	22.9	41.8	21.0	14.3		4.7
		230	60	2.10	25.7	33.0	22.5	18.8		4.4

[a] Measured by oxygen consumption at 450 °C. [b] (Specified species formed/total hydrocarbons formed) × 100. [c] (CO_2 formed/CO converted) × 100. [d] $\sum_j$ [(% selectivity of j species) × (number of carbon atoms in j species)]/100.

catalyst, Co/X, was found to be *ca.* 15 nm when estimated by the X-ray line-broadening analysis while CoX-Na did not show any cobalt peak because of severe line broadening, suggesting that the particle size is less than 3 nm.

Striking results can be seen in the selectivity patterns. The ion-exchanged CoX produced mainly methane, and the cobalt impregnated Co/X produced various hydrocarbons including an appreciable amount of branched hydrocarbon isomers. When compared with the above two catalysts, the sodium-treated CoX-Na showed a big suppression for the production of both methane and branched hydrocarbon isomers and an enhancement for the production of linear hydrocarbons (alk-1-enes and n-alkanes of C_2^+). Selectivity for alk-1-ene was very high when reaction pressure was kept low. Products formed over CoX-Na had higher average carbon number than those over Co/X; hydrocarbons in the range C_1–C_{22} are formed over CoX-Na while those in the range C_1–C_8 are formed over Co/X.

Although not shown here, analysis of the selectivity pattern of CoX-Na showed that alk-1-enes are produced in the range C_2–C_{14} with a maximum around C_4–C_7 while n-alkanes and branched hydrocarbons are mainly observed in the range C_8–C_{20} with maxima around C_{12}–C_{14}. Noteworthy is the fact that the sodium-treated catalyst, CoX-Na, did not show any noticeable deactivation during 3 days of reaction at reaction temperatures below 300 °C.

The sodium injection method is a simple but reliable technique to generate reduced cobalt particles inside a zeolite cage. The catalyst, CoX-Na, has relatively low turnover frequency; *i.e. ca.* $1 \times 10^{-4}\ s^{-1}$ at 230 °C when the dispersion of cobalt is assumed to be 100%, but its activity is as high as that of the impregnated catalyst (Co/X) when the activity is compared on the basis of per g of catalyst. We believe that the catalyst could be a potential candidate for commercial application owing to its strong resistance to sintering and high selectivity toward linear hydrocarbons, specifically towards alk-1-enes.

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