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Hydration–Decomposition of Styrene over Group IIB Oxide-Alumina Catalysts

A New Catalytic Water–Hydrocarbon Reaction System

The use of water as a hydrogen source in hydrocarbon conversion processes was the objective of previous studies that examined noble metal-catalyzed water–hydrocarbon cracking reactions (*1*, *2*). Noble metal catalysts preserve aromatic ring structures but gasify nonaromatic portions of the feed to cause low liquid yields (*1*). They are also sulfur sensitive (*3*). A new approach to a more selective reaction system was first to functionalize selected carbons of the feed with oxygen-containing groups, followed by selective steam reforming of those carbons using nonnoble metal catalysts to produce CO_2 and hydrocarbon fragments. This paper describes a new class of selective water–hydrocarbon reactions catalyzed by Group IIB catalysts.

EXPERIMENTAL

Alumina supported catalysts were prepared by impregnating freshly calcined alumina of 178 m^2/g surface area and 20–40-mesh size with aqueous solutions containing $Cd(NO_3)_2$, $Zn(NO_3)_2$, and/or KNO_3, followed by drying and calcining in air at 500°C. The final catalysts, each containing 1.0 mg-atom of metal in the oxide form per gram of material, were white in appearance and contained amorphous metal oxide components. The unsupported ZnO and CdO catalysts were reagent grade powders with surface areas of 2.1 and 1.4 m^2/g, respectively. A CdS/Al_2O_3 catalyst was obtained by sulfiding a 13% CdO/Al_2O_3 catalyst with a gas mixture containing 6% H_2S, 38% H_2O, and 56% He at 480°C. The orange product was analyzed to have a S/Cd atm ratio of 0.96. The reactions were carried out at 1 atm total pressure, using a micro-reactor that was described previously (*1*). Benzophenone was pumped as a melt through a heated line. After 30 min from the start of the feed introduction, 1-hr samples were collected in a trap cooled at −78°C, while the composition of the exit gas stream was constantly monitored by GC using a Porapak Q column. Each liquid sample was warmed to room temperature, the aqueous layer was saturated with salt, a measured amount of GC standard was added, and finally the sample was extracted with diethyl ether. The GC analyses were performed on a silicon oil DC 550 column.

HYDROLYSIS OF KETONES

The possibility that carbons bearing oxygen functions might be easily converted to CO_2 was tested using benzophenone as a model oxygenated compound. Group IIB oxides were chosen as potentially effective catalysts based on their known activities in the Henkel reactions, which will be discussed later. Over alumina support CdO and ZnO catalysts, benzophenone reacts with water exclusively by

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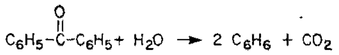
Eq. (1):



$$C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5 + H_2O \rightarrow 2\,C_6H_6 + CO_2 \qquad (1)$$

The liquid mixtures contained only the unreacted starting materials and benzene, while the amount of CO_2 evolved was usually 95 ± 5% of the stoichiometric amount based on Eq. (1). The CdO/Al_2O_3 catalyst is particularly effective, giving 95% conversion at 405°C under the conditions specified in Table 1, which also lists the activities of other supported and unsupported catalysts.

The high activity of the CdO/Al_2O_3 catalyst is interesting in view of the essential inactivities of the individual components when separated. Assuming that an exposed metal ion corresponds to an active site, the supported catalysts have a maximum site concentration of 1.0 mmol/g. For the unsupported catalysts even exposure of principal crystal planes were assumed to obtain 1.2×10^{15} Zn/cm^2 and 8.3×10^{14} Cd/cm^2, which in combination with the BET surface areas led to 0.042 mmol sites/g for ZnO and 0.019 for CdO. Using these estimated values, the turnover numbers were calculated as shown in Table 2. The trend of activity enhancement by support on alumina is evident, particularly with the CdO system, which gives more than two orders of magnitude acceleration of rate. In the study of the noble metal/Al_2O_3 catalysis in water–toluene reaction, Grenoble observed that alumina is not an inert support but an active participant in the rate-determining process as a water activator (*2b*). The present observation may provide another case for such a mechanism, or it may be due to changes in the nature of sites brought about by supporting. The latter possibility is discussed below.

TABLE 1

Benzophenone–Water Reaction over Oxide Catalysts[a]

Catalyst	BET area (m^2/g)	Temperature (°C)	Conversion[b] (%)
Al_2O_3	178	454	1.1
CdO	1.4	455	0.015
ZnO	2.1	450	0.25
12.8% CdO/Al_2O_3		405	94.7
8.1% ZnO/Al_2O_3		456	21.5
4.7% K_2O/Al_2O_3		451	3.6
12.8% CdO–4.7% K_2O on Al_2O_3		404	41.8[c]

[a] In each run 1.0 g of catalyst was used with a benzophenone feed rate of 11.8 mmol/hr and a H_2O/benzophenone/He (carrier gas) mole ratio of 18.8/1.0/3.0.

[b] Tabulated based on recovered materials.

[c] Trace amount of biphenyl was also formed.

TABLE 2

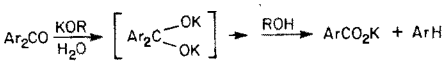
Comparison of Estimated Specific Activities of Al_2O_3-Supported and Unsupported Group IIB Oxide Catalysts

	$10^3 \times$ turnover number[a] at 453 ± 3°C	
	Al_2O_3-supported	Unsupported
CdO	>18[b]	0.03
ZnO	>0.72	0.20

[a] Moles of feed converted/moles of metal sites × sec. For estimations of the metal site concentrations, see text.

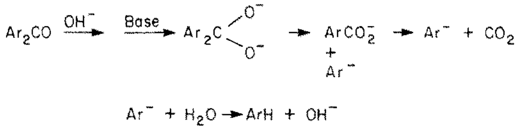
[b] Extrapolated from other temperatures.

Aromatic ketones are reported to undergo ready cleavage by the action of a mixed potassium t-butoxide–H_2O reagent in ether solvents (*4, 5*). The rate-determining step was proposed to involve the formation/decomposition of a dianion intermediate, **I**.



I

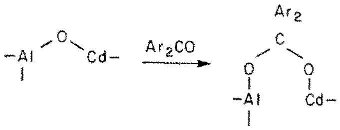
It is also known that cadmium salts are active catalysts in the Henkel reaction (disproportionation of alkali salts of aromatic carboxylic acids under a CO_2 environment). The catalytic action was generally ascribed to the ability of Cd(II) to decarboxylate $ArCO_2K$ to Ar^-K^+ (*6–9*). Thus, a combination of a base and a cadmium catalyst is expected to give a sequence of following steps:



$$Ar_2CO \xrightarrow{OH^-} \xrightarrow{Base} Ar_2C\begin{smallmatrix}O^-\\O^-\end{smallmatrix} \rightarrow ArCO_2^- + Ar^- \rightarrow Ar^- + CO_2$$

$$Ar^- + H_2O \rightarrow ArH + OH^-$$

In the present system the occurrence of a similar type of mechanism is plausible. It then becomes attractive to propose the formation of a surface Al–O–Cd group as an active site which can lead to a dianion intermediate, **II**. The absence of any trace amount of benzoic acid in the product mixture as well as the previous assessment that the rate is independent of ketone partial pressure (*3*) would then suggest that the decomposition of **II** corresponds to the overall rate-determining step.



II

WATER–OLEFIN REACTIONS OVER GROUP IIB CATALYSTS

It was shown that a clean hydrolysis reaction of ketones occurs on Group IIB oxide/Al_2O_3 catalysts to give hydrocarbon fragments and CO_2. One way of introducing oxy-functions to hydrocarbons is by hydration of olefinic bonds, and this is the basis for the process of converting alkenes to ketones by the action of $H_2O–O_2$ mixture over SnO_2/MoO_3 (*9–11*) and other catalysts (*12, 13*). For the present purpose a direct reaction between a model compound, styrene, and water was examined, and the results are summarized in Table 3.

Over the CdO/Al_2O_3 catalyst, styrene undergoes 43% conversion at 480°C to almost equal amounts of benzene, CO_2, CH_4 and H_2, a strong indication that

TABLE 3

Styrene–Water Reactions over Group IIB and Rhodium Catalysts[a]

Catalyst wt% on Al_2O_3	Temperature (°C)	Conversion (%)	100 × moles of product/mole of feed converted[b]								
			Benzene	Toluene	Et-benzene	Phenol	Aceto-phenone	CO_2	CH_4	H_2	CO
12.8 CdO	480	42.8	83.2	5.2	5.4	1.2	1.6	96.7	92.9	83.5	2.7
12.8 CdO/4.7 K_2O	480	4.6	2.3	88.2	4.4	1		88	2	76	37
14 CdS	480	21.3	54.7	3.6	19.6	4.8	16.3	62.8	35.9	142	3.9
10 ZnO	480	2.3	93.5	5.2	3.0						
	550	24.5	88.0	3.9	7.0	—	—	85.9	56.8	124	11
0.6 Rh[c]	400	4.4	68.1	7.9	17.2	—	—	62	—	270	133

[a] In each run, 2.0 g of catalyst was used with styrene feed rate of 17.4 mmol/hr and a H_2O/Styrene/He (carrier gas) mole ratio of 6.4/1.0/2.1.

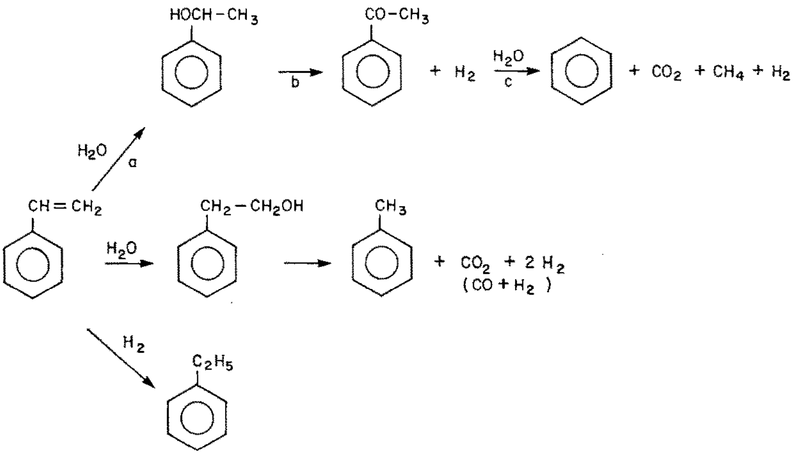
[b] Tabulated based on materials recovered in 30 to 90 min of reaction time.

[c] The amount of catalyst used was 0.30 g.

reaction (2) is actually taking place with a high selectivity:

$$C_6H_5CH{=}CH_2 + 2H_2O \rightarrow C_6H_6 + CO_2 + CH_4 + H_2 \quad \Delta G_{700} = -24.4 \text{ kcal/mol.} \qquad (2)$$

The product mixture also contained minor amounts of toluene, ethylbenzene, phenol and acetophenone. Although the exact origin of phenol is not clear at this time, the paths leading to other products may be represented by the following scheme:



In the run with a CdO–K_2O/Al_2O_3 catalyst a much lower conversion of 4.6% was obtained as compared to 43% achieved in the base case. This was brought about primarily by the drastic reduction in the amounts of benzene and acetophenone while the amount of toluene remained relatively constant. It can be estimated that the alkali addition suppresses the path to benzene by more than two orders of magnitude in rate. On the other hand, it was previously observed that the activity of a CdO/Al_2O_3 catalyst in the ketone hydrolysis reaction does not vary greatly by potassium doping. This suggests that the alkali addition selectively inhibits the step leading to the ketone intermediate, which corresponds to the acid-catalyzed hydration step a. Efficient scavenging of acid sites by alkali accounts for the observations, and thus, CdO/Al_2O_3 is a bifunctional catalyst. As step c was previously suggested to involve carbanion intermediates, we may be dealing with an amphoteric system.

The CdO/Al_2O_3 catalyst is unstable under a reducing environment, as indicated by the following equation:

$$CdO + H_2 \rightarrow Cd(l) + H_2O \quad \Delta G_{700} = +4.5 \text{ kcal/mol.}$$

A controlled experiment showed that in a fast flow of H_2 more than 95% of cadmium was volatalized in 1 hr at 480°C, depositing a flaky mirror at the bottom of the reactor. Under the reaction condition, the rate of loss is slower due to the presence of water, but still extensive; the spent catalyst after 3.5 hr of reaction contained 4.5% Cd (as metal). This corresponds to 60% cadmium loss. The activity–selectivity profile during this period is shown in Fig. 1. The relatively steady rate of conversion is rather striking in view of the catastrophic rate of cadmium loss. This can be rationalized by assigning the initial hydration reaction as the rate-determining step in the path leading to benzene. The effects of cadmium loss are revealed in the selectivity plots which show a sharp decrease in the amount of toluene produced as well as an increase of acetophenone with time. This is consistent with a view that all the reaction steps

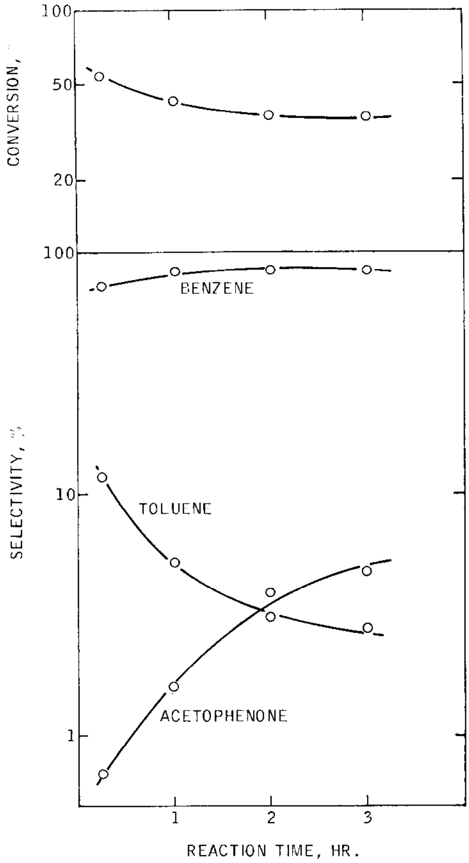


FIG. 1. Styrene–H_2O reaction over a CdO/Al_2O_3 catalyst at 480°C. Sixty percent of the original CdO was lost during the 3.5-hr reaction period.

excluding a are catalyzed by sites involving the metal oxide component.

An attempt was made to stabilize the CdO/Al_2O_3 system by sulfiding. The CdS/Al_2O_3, thus obtained, was found to retain cadmium under the reaction condition and gave a reasonably high activity. The selectivity was, however, not as specific, the pattern indicating that the function of metal site has shifted toward intensified hydrogenation–dehydrogenation activities. The ZnO/Al_2O_3 catalyst was found to be marginal in activity, which was tentatively attributed to its reduced hydration activity.

For comparative purposes, a run with a Rh/Al_2O_3 catalyst was also conducted. At 400°C, the turnover number to combined benzene and toluene products was determined to be 9.3×10^{-3} molecules/Rh·sec, and the ratio of side-chain cracking to total gasification, about 90/10. These figures are comparable to those obtained in the toluene–water reactions (*1, 2*), a turnover number to benzene of 13.5×10^{-3} and a selectivity to benzene of 83%. Apart from the question of whether or not the side-chain cracking occurs through a hydrogenated intermediate (*14*), this observation as well as the absence of oxygenated products and methane are consistent with the hydrogenolysis-type mechanism for the rhodium-catalyzed reaction.

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