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LETTERS

Catalytic Oxidation by Oxide Radical Ions. 1. One-Step Hydroxylation of Benzene to Phenol over Group 5 and 6 Oxides Supported on Silica Gel

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Catalytic oxidations of benzene by N_2O and O_2 and stoichiometric reactions of benzene with oxygen radicals including O^- and O_2^- have been investigated over various metal oxides. It has been clarified that N_2O leads the oxidation of benzene to phenol in the presence of water while O_2 causes the scission of carbon–carbon bonds of benzene to give maleic acid or maleic anhydride. The O^- and O_2^- species are suggested to be active oxygens in the former and the latter reactions, respectively. Vanadium oxide supported on silica gel was the best catalyst for phenol production among the catalysts examined here; the selectivity for phenol has attained approximately 70% at 10% conversion levels of benzene on 3.3 wt % V_2O_5/SiO_2 at 823 K.

Introduction

Recently individual properties of oxygen species on solid catalysts have appreciably been investigated to clarify the roles and/or functions of oxygen species in catalytic oxidation processes. It has been reported that the O^- species shows higher reactivity toward alkanes and alkenes than O_2^-, O_3^-, and O^{2-};[1-3] for example, O^- reacts even with methane at room temperature over various metal oxides.[1,4] The reaction intermediates and the products during the stoichiometric reactions of oxygen species with hydrocarbons are strongly dependent on the species.[3] The O^- ion can be formed by surface decomposition of N_2O in the presence of available electrons,[5] so that catalytic oxidation reactions of hydrocarbons using N_2O as an oxidant are of interest in connection with usual oxidations by O_2. Recent reports have indeed demonstrated that N_2O is an effective oxidant in the oxidative dehydrogenation of ethane[6] or in the partial oxidation of methane to methanol or formaldehyde.[7]

We wish here to report a new type of catalytic reaction in which benzene is catalytically oxidized to phenol by

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using N_2O as an oxidant in the presence of water vapor over group 5 and 6 oxides supported on silica gel, especially V_2O_5/SiO_2. This reaction is remarkably different from the well-known oxidation of benzene to maleic anhydride by O_2 catalyzed by various metal oxides.[8] Although the direct oxidation of benzene to phenol is possible through liquid phase oxidations,[9] uncatalytic gas-phase oxidations at elevated temperatures,[10,11] and newly developed photocatalytic oxidations,[12] as far as we are aware, little success has been achieved in obtaining directly phenol in a substantial amount through heterogeneous catalysis. The results presented in this Letter will show a change in the reaction paths of benzene depending on the oxidants and shed more light on the chemistry of active oxygen species.

Experimental Section

Unsupported metal oxide catalysts were prepared by calcining metal salts in air at 873 K for 5 h. Supported catalysts were prepared by impregnating silica gel (Fuji-Davison Chemical, ID-type) or other supports with ammonium metavanadate, ammonium paramolybdate, or ammonium paratungstate and calcined under the above conditions. The catalytic oxidation was followed in a continuous flow reactor at atmospheric pressure. The reactor containing 1.0 g of catalyst in a 15-mm i.d. quartz tube was connected to a Liebig's condenser, thus the product phenol could rapidly be quenched so that subsequent gas-phase reactions were prevented. In the experiment, helium gas was used as a diluent. Benzene and water were introduced from respective syringe pumps and evaporated in a preheated oven. A steady-state reaction was achieved for reaction times greater than about 2 h. The reactants and products were analyzed by gas chromatography.

Results and Discussion

Results summarized in Table I show that phenol is a major product at moderate conversions when using N_2O as an oxidant. While V_2O_5, MoO_3, and WO_3 were active for the phenol synthesis, other metal oxides catalysts such as MgO, MnO_2, Fe_2O_3, Co_3O_4, and NiO yielded solely carbon monoxide and carbon dioxide though their catalytic activities were relatively high. Under the same experimental conditions, silica gel was an order of magnitude less active. The apparent activation energies for the phenol production under the experimental conditions were 62.8, 82.9, and 58.6 kJ·mol^{-1} on 3.3 wt % V_2O_5/SiO_2, 5.0 wt % MoO_3/SiO_2, and 6.0 wt % WO_3/SiO_2, respectively.

TABLE I: Catalytic Oxidation of Benzene by Nitrous Oxide over Various Metal Oxides[a]

catalyst		reaction		selectivity,[d] %	
oxide	content, wt %	temp, K	convn,[c] %	C_6H_5OH	CO + CO_2
V_2O_5 [b]	100	873	3.9	0.2	98.6
V_2O_5/SiO_2	1.0	823	8.0	48.8	49.8
	3.3	823	11.3	45.2	53.8
	4.2	823	12.4	32.1	67.0
	7.2	823	12.0	30.6	68.7
	8.0	823	10.1	33.5	66.2
	13.6	823	6.5	17.8	81.7
	29.8	823	6.9	4.6	94.5
$V_2O_5/\gamma\text{-}Al_2O_3$	5.3	823	12.9	0.2	99.8
V_2O_5/MgO	5.1	823	3.6	1.7	97.0
$V_2O_5/\alpha\text{-}Al_2O_3$	5.1	773	0.04	0	100
V_2O_5/TiO_2	5.2	823	0.9	0	100
MoO_3 [b]	100	873	0.3	25.9	48.3
MoO_3/SiO_2	5.0	873	1.2	81.0	15.8
WO_3 [b]	100	873	1.5	3.0	88.1
WO_3/SiO_2	6.0	873	5.2	40.8	57.9

[a] The catalytic run was carried out under the following conditions: catalyst weight 1.0 g, total flow rate of gases 60 cm^3·min^{-1}, partial pressure: C_6H_6, 8.2; N_2O, 20.3; H_2O, 20.3; He, 52.5 kPa. [b] In these experiments, unsupported metal oxides were used as the catalysts. [c] Based on benzene introduced into the reactor. Values were those at steady state. [d] Based on benzene reacted. Small amounts of fumaric acid, maleic acid, and C_1–C_4 hydrocarbons were observed in some cases.

Among V_2O_5, MoO_3, and WO_3, V_2O_5 was the most effective catalyst for the formation of phenol, so that the effects of supports and V_2O_5 content on the reaction were investigated (Table I). With γ-alumina or silica gel as a support, the catalytic activity of V_2O_5 was the highest. However, most of the reaction products over the $V_2O_5/\gamma\text{-}Al_2O_3$ catalyst were CO and CO_2. The V_2O_5/MgO catalyst showed medium catalytic activity and had the ability to give a small amount of phenol. When vanadium oxide was supported on α-alumina or titania, the catalytic activity was the lowest and little phenol could be formed even at such low conversions. These results indicate a strong interaction between vanadium oxide and the supports which influences the course of the oxidations. Much effort has been devoted to the characterization of vanadium oxide on various supports by several investigators,[13] but the marked effect in the present system is not explicable; further experiments are currently underway to elucidate the effect of supports. The correlation between the V_2O_5 content on silica gel and catalytic activities was also shown in Table I. It is clear that 1–10 wt % V_2O_5 content was effective for phenol formation and the maximum yield of phenol was achieved at 3.3 wt %.

As shown in Table II, the presence of water is essential for phenol formation and the amount of phenol increases with increasing amounts of water. Approximately constant levels of conversion of benzene independent of the partial pressures of water suggest that water would act as an inhibitor toward the consecutive oxidation of phenol. On the other hand, too high pressure of nitrous oxide resulted in a decrease of in the phenol yield. It would be noteworthy that when O_2 was used as an oxidant instead of N_2O under similar experimental conditions over 3.3 wt % V_2O_5/SiO_2, significant amounts of maleic acid and fumaric acid and a trace amount of phenol were observed, in

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TABLE II: Dependence of the Phenol Synthesis over the 3.3 wt % V_2O_5/SiO_2 Catalyst on the Partial Pressure of Gases Feeded[a]

partial press.,[b] kPa			convn,[c] %	selectivity,[d] %	
C_6H_6	N_2O	H_2O		C_6H_5OH	CO + CO_2
8.2	16.9	0	10.4	6.8	92.4
8.2	16.9	12.3	11.7	22.1	76.1
8.2	16.9	20.3	9.2	62.4	36.5
8.2	16.9	30.7	10.7	71.5	27.6
8.2	16.9	40.5	9.4	68.7	29.8
8.2	10.1	20.3	7.8	44.5	54.3
8.2	13.5	20.3	7.3	51.9	46.4
8.2	20.3	20.3	11.3	45.2	53.8

[a] Reaction temperature was 823 K. [b] Total flow rate: 60 $cm^3 \cdot min^{-1}$, balance: helium. [c] See footnote c, Table I. [d] See footnote d, Table I.

agreement with the well-known oxidation of benzene to maleic anhydride by O_2 in the absence of water.[8]

The stoichiometric reactions of benzene with oxygen radicals adsorbed on the 3.3 wt % V_2O_5/SiO_2 catalyst were studied in a conventional closed system to reveal the active oxygen species. The catalyst was reduced in 100 torr of H_2 at 773 K for 30 min. The partially reduced catalyst contained V^{3+} and/or V^{4+} on the surface, which upon exposure to N_2O or O_2 gave O^- or O_2^- ions according to reaction 1 or 2. In the presence of benzene the O^- ions,

$$N_2O + V^{3+} \text{ (or } V^{4+}) \rightarrow V^{4+}O^- \text{ (or } V^{5+}O^-) \qquad (1)$$

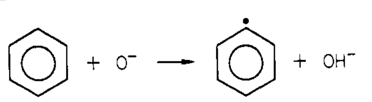
$$O_2 + V^{3+} \text{ (or } V^{4+}) \rightarrow V^{4+}O_2^- \text{ (or } V^{5+}O_2^-) \qquad (2)$$

characterized by an ESR spectrum having $g_\perp = 2.025$ and $A_\perp = 13.7$ G,[14] decayed with a half-life of 5 min at 233 K and rapidly at 298 K, though no new radicals were detected. The reaction products of O^- ions with benzene were followed by analyzing the gas phase after desorption or decomposition of the surface species upon heating slowly the sample to 773 K. Phenol, together with carbon dioxide and fumaric acid etc., was observed as the product. In contrast, the O_2^- ions with $g_1 = 2.022$ ($A_1 = 9.9$ G), $g_2 = 2.011$ ($A_2 = 6.4$), and $g_3 = 2.002$ ($A_3 = 4.1$)[14] did not react with benzene at 298 K and reacted slowly at 373–423 K. Maleic anhydride was detected in the reaction products but phenol was not obtained. These results were qualitative but clearly indicate that the reaction path of benzene is dependent on the kinds of active oxygen species. It is suggested that oxidation of benzene with O_2^- causes scission of carbon–carbon bonds while O^- causes nondestructive oxidation to phenol and that O^- is more reactive than O_2^-. A similar conclusion has been reported previously for a study of stoichiometric reactions of oxygen radicals on MgO with alkanes and alkenes.[1,3] However, MgO-catalyzed oxidation of benzene by N_2O did not yield phenol. Apparently, the stability and/or reactivity of the intermediate resulting from the initial reaction of O^- with benzene are dependent on the surface properties of the catalyst oxides.

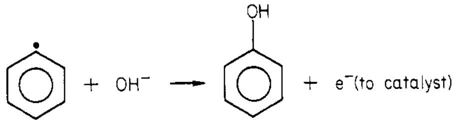
We believe that our results are best rationalized by either of the following two schemes. As has been suggested

$$N_2O + e^-\text{(from catalyst)} \rightarrow O^- + N_2 \qquad (3)$$

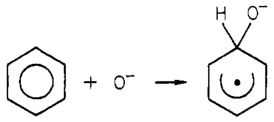
by several workers,[1,4,6,15] the O^- ion has been postulated as an active species in initiating the catalytic process via hydrogen abstruction reaction 4a. The formation of phenol may thus result from the reaction of the phenyl radical with a hydroxyl ion derived from a surface hydroxyl group or water (4b). One cannot, however, exclude the possibility that the reaction proceeds initially by the direct addition of O^- to benzene (5a), and then by forming a biradical intermediate (5b) which subsequently becomes stabilized by transition to phenol in gas phase (5c). Reaction 5c has been proposed by Sibener et al.[10] in gas-phase reaction.



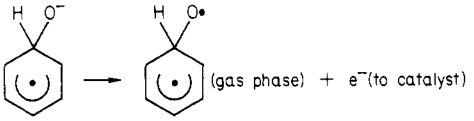
(4a)



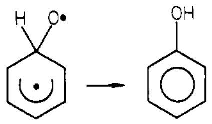
(4b)



(5a)



(5b)



(5c)

It is clarified that the use of nitrous oxide instead of molecular oxygen as an oxidant makes it possible to produce phenol directly from benzene in lieu of maleic anhydride. Phenol is produced by multistep procedures from benzene in industry.[16] Although phenol can also be formed by dehydrogenating oxygenated cyclohexanes[17] or by direct interaction of cyclohexanes with water,[18] the yields were very low in these reactions. Therefore, the present results not only are of significance for the chemistry of active oxygen species, but also provide the basis for the development of a new class of catalytic oxidation processes of importance to the petrochemical industry.

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Registry No. V_2O_5, 1314-62-1; MoO_3, 1313-27-5; WO_3, 1314-35-8; O^-, 14337-01-0; O_2^-, 11062-77-4; benzene, 71-43-2; nitrous oxide, 10024-97-2.

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(14) These values are in fair agreement with those in the literature. Shvets, V. A.; Kazansky, V. B. *J. Catal.* **1972**, *25*, 123. Yoshida, S.; Matsuzaki, T.; Kashiwaki, T.; Mori, K.; Tarama, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1564.

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