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Oxidation of Toluene to Benzoic Acid Catalyzed by Modified Vanadium Oxide

Wadood T. Mohammed
Chemical Engineering Department- College of Engineering- University of Baghdad

Abstract

A variety of oxides were examined as additives to a V_2O_5/Al_2O_3 catalyst in order to enhance the catalytic performance for the vapor phase oxidation of toluene to benzoic acid. It was found that the modification with MoO_3 greatly promoted the little reaction leading to improve catalyst performance in terms of toluene conversion and benzoic acid selectivity. The effect of catalyst surface area, catalyst promoters, reaction temperature, O_2/toluene, steam/toluene, space velocity, and catalyst composition to catalyst performance were examined in order to increase the benzoic acid selectivity and yield.

Introduction

The yield of benzoic acid in the vapor phase oxidation of toluene remains far from a commercial production level because of the low toluene conversion and the poor selectivity to benzoic acid. Although, a great number of studies of the reaction have been performed for years [1-10]. At present, vanadium oxide, commonly used for partial oxidation of aromatic hydrocarbons, is widely accepted as the active species which effectively yields benzoic acid and it is considered to be very difficult to enhance the benzoic acid yield which is about 30% at most. Recently, the mechanism of toluene oxidation in the vapor phase has been investigated by Anderson [4] and Zhu and Anderson [5] and its reaction network has become apparent with benzyle cation on the catalyst presented to be the precursor. However, it still has been an open question regarding a specific method on how to improve catalytic performance for the reaction.

In the present work, we tried to modify the locally prepared $V_2O_5.Al_2O_3$ catalyst with some oxides in order to improve the catalyst performance.

Experimental Work

1. Catalyst

100 g of $V_2O_5.MoO_3.Al_2O_3$ catalyst with a composition of 5 wt.% V_2O_5 and 5 wt.% MoO_3 was prepared by impregnation method. A commercially available α-alumina oxide was used as the carrier material. The carrier has macro-porous so that the specific surface area is relatively low, namely about 5 m^2/g. The carrier material was calcined for 24 h at a temperature of 1150 ˚C (1423 K) and then mixed with a water solution of NH_4VO_3 in such a proportion (8 g in 30 ml) that the solution could just be absorbed by the carrier material. The molybdenum was added by impregnation of $V_2O_5.Al_2O_3$ using the same procedure except that

the impregnation solution prepared by dissolving 6 g of ammonium molybdenum in 20 ml of deionized water (or 15 g of cobalt nitrate in 30 ml of water). Followed by drying at 120 ˚C for 2 hours and then calcining in air at 500 ˚C for 3 hr.

2. Apparatus and Procedure

The feed was heated prior to entrance into the reactor. The heating solution is divided into three separate sections; steam generator, air heater using heating tape, and round bottom flask heated by a mantle heater to heat the toluene. Heating is controlled by voltage regulators.

The oxidation reactor is made of QVF glass with an inner diameter of 2.54 cm and a length of 50-70 cm. The reactor is divided into two zones. The entrance zone (30 cm long), serving as a preheater section, was packed with glass balls. The reaction zone, the length of which depends on the space velocity, was packed with the catalyst. Both zones are heated with a heating tape controlled by a voltage regulator.

The oxidation products are cooled and condensed in two glass condensers in series and collected in a glass flask. Cooling is achieved by tap water. The temperature is measured in various locations along the system by thermocouples type J. While the toluene and steam were heated, the reaction zone was also heated up to the desired temperature in hot air flow, and then the feed introduced and mixed in the entrance of the preheating reactor section.

The oxidation products of unreacted toluene, benzoic acid, benzaldehyde, benzene, and other products were collected in a cold trap and analyzed by gas chromatography (PYE UNICAM) using thermal conductivity detector.

Results and Discussion

1. Effect of Catalyst Surface Area

It is obvious that the calcinations temperature is one of the most important factors which affect the catalyst activity, indicating that the low surface area causes a significant increase in the benzoic acid selectivity.

Appropriate surface area is revealed to be about 5 m^2/g to obtain best conversion and benzoic acid selectivity. These results suggest that an increase in micropores or mesopores of the catalysts is not effective for the selective formation of benzoic acid, implying that too strong adsorption of toluene in the micropores accelerates the complete oxidation to Co and Co_2. The drop in conversion at high calcinations temperature is obviously caused due to the decrease in surface area.

Optimum benzoic acid selectivity was obtained at the calcinations temperature of 1150 ˚C (1423K) as shown in Table l.

Table l, Results of experimental runs for different catalyst surface area effect*

Surface area m^2/g	Molar ratio toluene/air/steam	Space velocity h^{-1}	Conversion% Toluene	Selectivity%			
				Benzoic acid	Benzaldyhide	Benzene	Others
0.3	1/8/20	2100	27.2	62.5	17.7	14.5	5.9
0.3	1/10/30	2560	32.8	64.1	15.0	16.3	4.6
5	1/8/20	2050	42.1	64.5	16.2	14.2	5.1
5	1/10/30	2480	48.2	67.8	18.3	11.7	2.2
100	1/8/20	1995	58.1	38.1	35.8	24.0	2.1
100	1/10/30	2420	60.6	35.2	32.0	20.0	12.8
200	1/8/20	2080	65.4	30.5	40.2	20.2	9.1
200	1/10/30	2510	69.3	28.6	43.1	21.1	7.2

*Catalyst used $V_2O_5.MoO_3/Al_2O_3$ in the composition of 5 wt.% V_2O_5 and 5 wt.% $MoO_{3.}$ Calcination temp.: 1200, 1150, 700, and 350 ˚C respectively. Catalyst weight 100g. Reaction temp.: 350 ˚C (623 K)

2. Effect of Catalyst Promoters

Preferably, the catalyst to be used in the process comprises activating additives, in one compound of cobalt or molybdenum, beside the vanadium oxide.

Table 2 shows that molybdenum oxide was active than cobalt for the conversion of toluene and benzoic acid selectivity.

Table 2, Results of experimental runs for catalyst promoters effect*

Catalyst	Molar ratio toluene/air/steam	Space velocity h^{-1}	Conversion% Toluene	Selectivity%			
				Benzoic acid	Benzaldyhide	Benzene	Others
$V_2O_5.CoO_3.Al_2O_3$	1/8/20	2100	42.1	54.5	17.2	15.2	13.1
	1/10/30	2560	48.2	57.8	19.3	18.7	4.2
$V_2O_5.MoO_3.Al_2O_3$	1/8/20	2120	53.2	72.2	6.1	11.3	10.4
	1/10/30	2520	58.3	76.3	5.3	14.2	4.2

*Catalyst surface area, 5 m^2/g. Catalyst used $V_2O_5.Co_2O_3.Al_2O_3$ with 5 wt.% V_2O_5 and 5 wt.% Co_2O_3. $V_2O_5.MoO_3.Al_2O_3$ with 5 wt.% V_2O_5 and 5 wt.% MoO_3. Catalyst weight 100g. Reaction temp.: 350 ˚C.

3. Effect of Reaction Temperature

The results clearly demonstrate that increasing the reaction temperature up to 350 ˚C causes the conversion, benzoic acid selectivity to increase, beyond that the benzoic acid selectivity decrease.

Table 3 shows the effect of reaction temperature on catalyst activities. A gradual decrease in benzoic acid selectivity was probably due to the enhanced oxidation of benzoic acid to Co and Co_2.

Table 3, Results of experimental runs for reaction temperature effect*

Temp. ˚C	Conversion % Toluene	Selectivity%			
		Benzoic acid	Benzaldyhide	Benzene	Others
250	41.8	58.2	6.3	11.8	23.7
300	49.7	65.0	6.7	10.2	18.1
350	58.3	76.3	5.3	14.2	4.2
400	68.2	48.7	11.1	16.0	24.2

*Catalyst surface area, 5 m^2/g. Catalyst used $MoO_3.Al_2O_3$ with 5 wt.% V_2O_5 and 5 wt.% MoO_3. Catalyst weight 100g. Molar ratio (toluene/air/steam) of 1/10/30. Space velocity 2520 h^{-1}.

4. Effect of Oxygen Ratio

Figs. l and 2 exhibits the effect of the O_2/toluene molar ratio on catalytic activity with increasing molar ratio up to 2.52 (for air this ratio is 12) leading to a better catalytic performance both in benzoic acid selectivity and toluene conversion.

Complete combustion products appeared to increase above an oxygen molar ratio of 2.52.

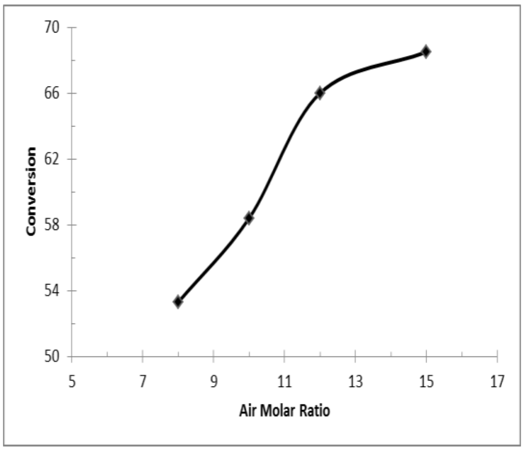

Fig. 1, Effect of Air Molar Ratio on Conversion of Toluene

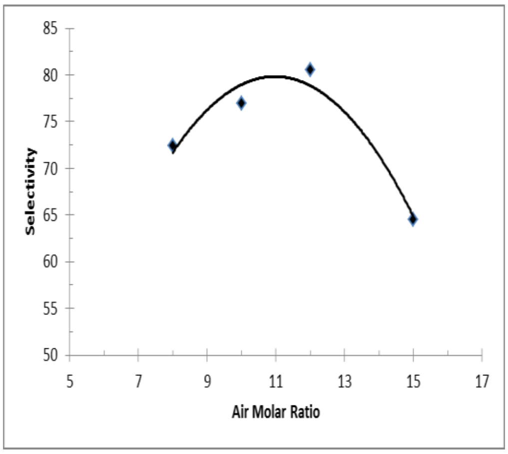

Fig. 2, Effect of Air Molar Ratio on Selectivity of Beenzoic Acid

5. Effect of Stream Ratio

The effect of water on the catalytic oxidation of hydrocarbons has been observed frequently. The results show that water addition improves both the activity and the selectivity to benzoic acid. It is suggested to be due to hydrolysis of adsorbed benzoate species at the higher concentration of surface hydroxyl groups caused by the water addition or directly by water.

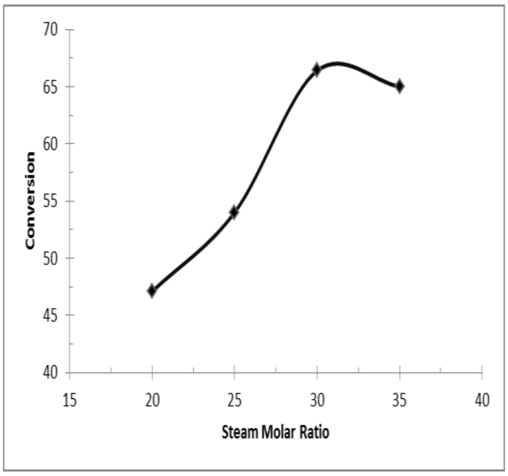

Fig. 3, Effect of Steam Molar Ratio on Conversion of Toluene

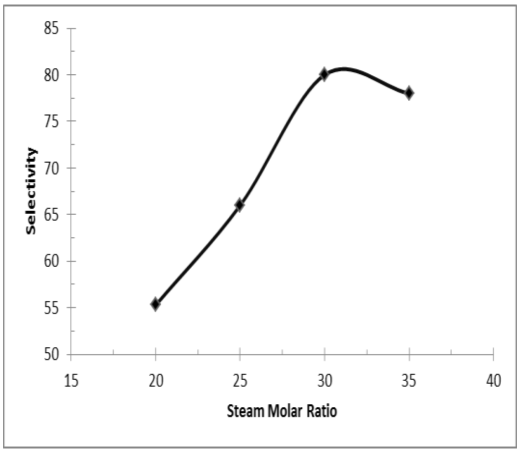

Fig. 4, Effect of Steam Molar Ratio on Selectivity of Toluene

Figs. 3 and 4 shows the effect of steam/toluene molar ratio on the catalyst activities. Toluene conversion and benzoic acid selectivity appeared small decrease a strem/toluene ratio of 30. While the benzoic acid selectivity showed a rapid decrease below steam/toluene molar ratio of 25.

6. Effect of Space Velocity

Table 4 exhibits the effect of the space velocity on catalyst performance. The toluene conversion decreased with a rise in space velocity.

It has been shown that with space velocities above 2450 h^{-1}, the desired product can be produced in good yield with short residence time. Moreover, the formation of oxidative decomposition is reduced to a minimum. It is therefore, generally possible to rise the space velocity to as much as approximately 2580 h^{-1} l gaseous feed / l cat.h.

Table 4, Results of experimental runs for space velocity effect*

Catalyst weight (g)	Space velocity h^{-1}	Conversion % Toluene	Selectivity % Benzoic acid	Benzaldyhide	Benzene	Others
50	3430	40.3	53.2	2.8	19.0	25
75	3160	51.1	70.8	3.1	16.1	10.8
100	2580	65.6	80.0	4.2	12.8	3
125	2318	69.1	69.3	11.8	15.0	3.9
150	1991	74.3	58.1	14.3	16.2	11.4

*Catalyst surface area, 5 m^2/g Catalyst used $V_2O_5.MoO_3.Al_2O_3$ with 5 wt% V_2O_5 and 5 wt% MoO_3, Reaction temp. 350 °C. Molar ratio toluene/air/steam 1/12/30.

7. Effect of Catalyst Composition

The results exhibit that small proportion of V_2O_5 and MoO_3 in the catalyst are required. It has been found that even as little as 5 wt% V_2O_5 and 5 wt% MoO_3 were sufficient for obtaining smooth conversion with good selectivity as shown in Table 5.

Table 5, Results of experimental runs for catalyst composition effect*

Catalyst Composition V_2O_5	MoO_3	Conversion % Toluene	Selectivity % Benzoic acid	Benzaldyhide	Benzene	Others
2	2	41.2	80.9	5.2	11.2	2.7
5	5	65.6	80.0	4.2	12.8	3
10	10	66.1	76.3	8.1	14.2	1.4

*Catalyst surface area, 5 m^2/g Catalyst used $V_2O_5.MoO_3.Al_2O_3$ with 5 wt% V_2O_5 and 5 wt% MoO_3, Reaction temp. 350 °C. Molar ratio toluene/air/steam 1/12/30. Space velocity 2580 h^{-1}.

Conclusions

Great enhancements of catalyst performance has been achieved by the modification of $V_2O_5.Al_2O_3$ with MoO_3 addition of 5 wt% of MoO_3 to a V_2O_5. Al_2O_3 catalyst is revealed to be effective for the enhancement of catalyst performance in terms of toluene conversion and benzoic acid selectivity. But other additives such as Co_2O_3 showed no improvement of the $V_2O_5.Al_2O_3$ catalyst performance.

The best reaction conditions are: molar ratio of toluene to air to steam, space velocity, and reaction temperature are 1/12/30, 2580 h^{-1}, and 350 °C respectively.

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