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Bulletin of Chemical Reaction Engineering & Catalysis, 16 (1) 2021, 1-8

Research Article

Study on Ammonia-induced Catalyst Poisoning in the Synthesis of Dimethyl Oxalate

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Received: 30th November 2020; Revised: 2nd January 2021; Accepted: 6th January 2021
Available online: 21st January 2021; Published regularly: March 2021

Abstract

On an industrial plant, we observed and examined the ammonia-poisoning catalyst for the synthesis of dimethyl oxalate (DMO). We investigated the catalytic activity in response to the amount of ammonia and revealed the mechanism of such poisoning by X-ray photoelectron spectroscopy (XPS) characterization. Our results show that only 0.002% ammonia in the feed gas can significantly deactivate the Pd-based catalyst. Two main reasons were proposed: one is that the competitive adsorption of ammonia on the active component Pd hinders the carbon monoxide (CO) coupling reaction and the redox cycle between Pd^0 and Pd^{2+}; and the other is that the high-boiling nitrogen-containing amine compounds formed by reacting with ammonia have adsorbed on the catalyst, which hinders the progress of the catalytic reaction. The deactivation caused by the latter is irreversible. The catalytic activity can be completely restored by a low-temperature liquid-phase in-situ regeneration treatment.

Keywords: dimethyl oxalate; synthetic catalyst; ammonia poisoning; space-time yield; regeneration

How to Cite: H.-W. Liu, S.-T. Qian, E.-F. Xiao, Y.-J. Liu, J. Lei, X.-H. Wang, Y.-H. Kong (2021). Study on Ammonia-induced Catalyst Poisoning in the Synthesis of Dimethyl Oxalate. *Bulletin of Chemical Reaction Engineering & Catalysis*, 16(1), 1-8 (doi:10.9767/bcrec.16.1.9572.1-8)

Permalink/DOI: https://doi.org/10.9767/bcrec.16.1.9572.1-8

1. Introduction

The gas-phase synthesis of ethylene glycol based on the oxalate route was firstly industrialized in China [1-2]. At present, an ethylene glycol plant with an annual output of nearly 5 million tons has been conceived, and a promising plant (under construction) is expected to be of an annual output as high as more than 10 million tons per year [3-4]. The process mainly involves a two-step reaction. First, CO and methyl nitrite CH_3ONO (MN) are carbonylated to dimethyl oxalate (DMO) in the presence of Pd/α-Al_2O_3 catalyst, and then with a copper-based catalyst the refined DMO is converted into ethylene glycol (EG) through hydrogenation [5-10]. After more than 50 years of research and more than 10 years of industrialization, this process has gradually matured [11-14]; however, in-depth research on industrial applications and reaction processes are still needed. It is difficult for the existing large-scale devices to achieve long-term cycles of full load and stable operation, because the main problem lies in two key factors in the catalyst, *i.e.* DMO synthesis and hydrogenation [15-18]. For instance, how to further reduce operating costs as for Pd-based synthesis catalyst [19,20], or how to avoid pulveri-

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zation and coking as for copper-based hydrogenation catalysts in order to extend the catalyst life [21].

The catalyst for DMO synthesis is generally a Pd-based catalyst supported by macropores α-Al_2O_3 [22-25]. The selectivity of such catalyst is usually as high as 99% or above. The activity is defined by the space-time yield under the conditions of the followings: reaction temperature of 100～140 °C, space velocity of 2000～4000 h^{-1}, and the MN content of 10～15%. Since the carbonylation between CO and MN is a super exothermic reaction and self-decomposition of MN may occur when temperature exceeds 150 °C, the focus of the existing research is mainly on the improvement of the catalyst's low-temperature activity, the control of the reaction process, and the safety of the system [26-30]. There are relatively few basic researches on the application of catalysts [31,32]. For example, the study on the influence of ammonia on synthesis catalysts. Gao and Wu [33,34] have studied on the ammonia poisoning of Pd-based catalysts for the synthesis of DMO. It is believed that 0.54% of ammonia content only causes a decrease in catalyst activity but does not cause complete deactivation. X-ray photoelectronic energy spectrometer (XPS) and other related characterization analysis revealed that the competitive adsorption of ammonia molecules on the active Pd^{2+} hinders the oxidation-reduction cycle of the latter, resulting in a decrease in catalyst activity. Interestingly, we have observed that in an industrial plant setting the trace amount of ammonia in the CO gas source leads to significant catalyst deactivation. Furthermore, we combined laboratory simulation and characterization analysis of poisoned catalyst to reveal the mechanism of the poisoning and regeneration.

2. Materials and Methods

2.1 Catalyst Preparation

The Pd-series catalyst for DMO synthesis was synthesized according to our previous method [35], which was used for a commissioning run test of 200,000 tons per year ethylene glycol industrial plant in 2015. Briefly, spherical α-Al_2O_3 carriers were loaded with $PdCl_2$ through impregnation, and then reduced (by hydrazine hydrate), rinsed, and dried at 120 ℃.

2.2 Catalyst Activity Evaluation

The evaluation of catalyst activity was carried out on atmospheric fixed-bed reaction device: the internal diameter of the stainless steel reaction tube is 8 mm; the catalyst filling volume is 1 mL; the reaction space velocity is 3000 h^{-1}; the reaction temperature is 100～130 ℃; and the carrying gas composition (V/V) is 20%CO+10%CH_3ONO+70%N_2. We examined the amount of NH_3 that is added into the carrying gas and causes catalyst poisoning.

DMO products were collected through condensing the resulting reaction gas and weighted to calculate the space-time yield (STY) index of the catalyst. The composition of reaction gas (pre- and post-reaction) was analyzed using Agilent 7820 gas chromatography, equipped with TCD and FID dual detector, aiming at evaluating the conversion rate of CH_3ONO.

2.3 Characterization of the Catalyst

VG Multilab 2000 X-ray photoelectronic energy spectrometer was used to determine the valence state and relative content of the elements on the surface of the catalyst. The test conditions were Al target, power of 300 W, and pass energy of 25 eV. The specific surface area of the catalyst was measured by Anton-Paar Autosorb-1-C-TCD-MS automatic physicochemical gas adsorption instrument, adopting a nitrogen adsorption method. The composition of DMO products (by-products, such as: dimethyl carbonate or methyl formate) were qualitatively analyzed by Thermo Fisher's Trace DSQ II gas chromatography-mass spectrometer.

3. Results and Discussions

3.1 Catalyst Poisoning

In the September of 2015, a newly built ethylene glycol plant with a production capacity of 200,000 tons per year was commissioned. The plant features a patented technology, *i.e.* WHB® Coal to Polymer Grade Ethyl Glycol New Technology [36]. Among them, the DMO synthesis system consists of two production lines (A/B, in parallel), each of which was filled with 50 cubic synthesis catalysts. In the commissioning test run stage, only production line B was deployed to use. After 20 days, the operating load was increased to 80%, and the hot spot temperature of the synthesis reactor stabilized at 117 °C. On the 25th day, we observed that the catalyst activity tended to be declining. After that, the catalyst hot spot temperature needed to be increased by 1 °C every 1-2 days to maintain catalyst activity and production load. On the 32nd day, the catalyst hot spot temperature was required to be 125 °C, which lasted for the next 4 days. The methyl nitrite conversion rate continued to decrease. On the 36th day, the production load had dropped to 20% of the full load, and the catalyst was nearly deactivated. The system was shut down for inspection.

It appeared that an acute poisoning on the catalyst was likely attributed to the described performance and the dysfunction of the catalyst. We had investigated the possible causes to the catalyst poisoning on-site. The main indicators of raw materials, including carbon monoxide, methanol, nitric acid, and oxygen, appeared to meet the process requirements. The purification unit in the primary process was found to contain excessive ammonia. The methanol that is used for the low-temperature methanol washing process of the purification unit contains an ammonia mass percentage as high as 0.027%, causing the volume percentage of ammonia in the carbon monoxide feedstock to be 17～20×10^{-6}(ppm). Normally, the standard indicator should be below 0.1×10^{-6}.

Gao *et al.* [33] simulated the changes in the activity of the Pd catalyst for the synthesis of diethyl oxalate (DEO) by the coupling reaction of CO and ethyl nitrite under different ammonia contents. The results showed that if the ammonia content does not exceed 0.54% the decrease of the activity of the DEO synthesis catalyst occurred. When the ammonia content reaches 1.16%, the activity decreases rapidly and then the catalyst became inactivated. At the industrial plant setting, however, we have observed that only 0.0017-0.002% ammonia exceeding the standard can cause significant catalyst deactivation. The effect of different ammonia content on the space-time yield of the Pd catalyst for the coupling reaction of CO and methyl nitrite was evaluated at the reaction temperature of 100 and 120 °C for 3 hours, respectively. The results are shown in Figure 1 (a/b).

As shown in Figure 1, 1200 ppm ammonia content can deactivate the DMO synthesis catalyst within 3 hours. As the ammonia content is reduced to 20 ppm, the test results showed that the catalyst activity can be reduced to below 50% within 12 hours. This indicates that ammonia shows more significant impacts on DMO synthesis catalyst than DEO synthesis catalyst, which is consistent with results from industrial plant testing.

3.2 Evaluation of the Activity of the Poisoning Catalyst

We sampled the catalyst in the industrial plant for the synthesis of DMO and evaluated its activity during the poisoning process. Since the DMO synthesis was carried out in a shell-and-tube isothermal reactor, the catalyst was packed in the tube with a filling height of 4 m. Therefore, we sampled at different positions in the reactor at different heights for evaluation analysis. Our results showed that no significant difference in catalyst activity among these sampling points (orientations and heights). We conducted laboratory activity evaluation, MN conversion rates, and space-time yields (STYs). For instance, we selected the samples that are 200, 800, 1500, and 3500 mm from the nozzle, which were noted as A, B, C, and D, respectively in Figure 2.

It can be seen from Figure 2 that four catalyst samples with different heights show significant decreases in STYs compared with the control sample. The STYs at 100 °C decreases from 557 g/L·h to 247~271 g/L·h, by about 54%. The STYs at 120 °C decreased from 698 g/L·h to 516~537 g/L·h, by about 25%. One could conclude that the catalyst demonstrates a uniform deactivation and the low-temperature activity

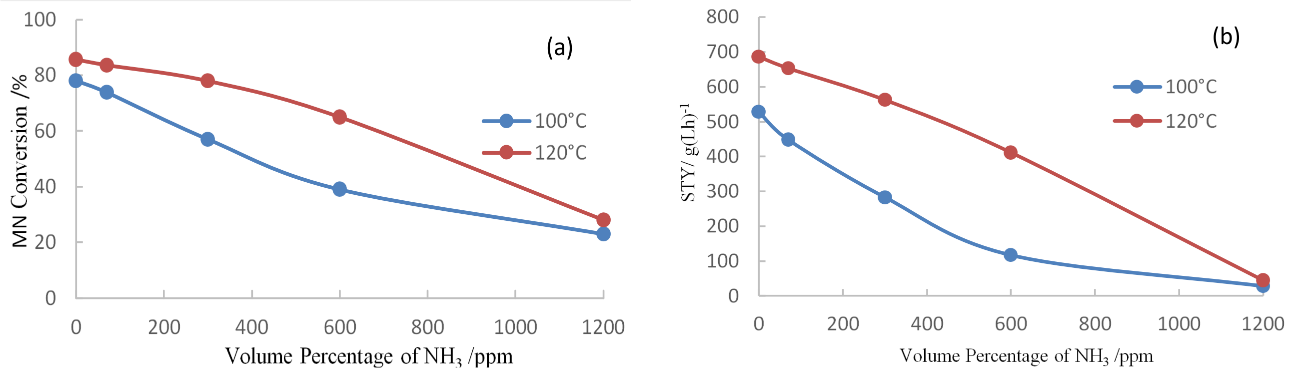

Figure 1. The effect of different ammonia contents on MN conversion (a) and STY (b) of DMO synthetic catalyst

loss was more significant, which was confirmed by the performance on the industrial plant.

3.3 Characterization of the Poisoning Catalyst

X-ray photoelectron spectrometer (XPS) was used to determine the valence state and relative content of the main elements on the surface of the catalyst for the samples (A), (B), and (C) that previously described. The results are shown in Table 1, Figures 3, and 4. The Pd catalyst for the synthesis of HDMO-1 DMO is in the reduced Pd, confirmed by the zerovalent Pd's characteristic peaks of Pd3d5/2 (binding energy of 335.3 eV) and Pd3d3/2 (binding energy of 340.3 eV) in the control sample (Figure 2). As for the poisoning catalyst samples, the two peaks shift to 336.3 eV and 341.3 eV, suggesting the formation of Pd (II). After peak splitting, the electron binding energy peaks of 397.4 eV and 401.3 eV were observed for Sample (A) in Figure 3. Similar peaks were resembled for Samples (B) and (C), whereas their atomic percentages were reduced by about 50%. Referring to the standards, the nitrogen-containing compound is likely to be $R\text{-}NH_2$ amine substance.

After conducting XPS research on Pd catalyst deactivated by ammonia poisoning in the coupling reaction of CO and ethyl nitrite, Wu *et al.* [34] believe that the competitive adsorption of ammonia molecules on the active component Pd^{2+} hinders the CO coupling reaction on the catalyst surface and the redox cycle of the active component Pd, resulting in a decrease in catalyst activity. After the ammonia molecules are desorbed, the activity can be partially restored. The reason for the irreversible ammonia poisoning is that the oxidized Pd^{2+} can not be reduced in the reaction system and the Pd coalescence occurs.

In the comparison of poisoning catalyst and the control characterized by XRD (Figure 5), we found no significant difference in the catalyst structure and active component dispersion. No changes in morphology was observed by TEM (images not shown). The observation results were further supported by the fact that we didn't observe the temperature steep rising during the operation. The BET analysis showed that the specific surface area of the poisoned sample was 9.1 m^2/g, which increases by

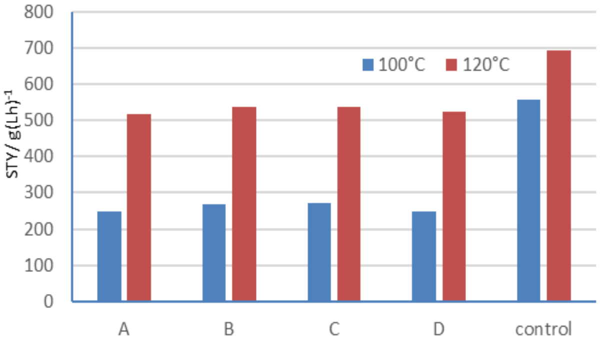

Figure 2. Comparison of the space-time yields of poisoning catalysts (A-D) and controls

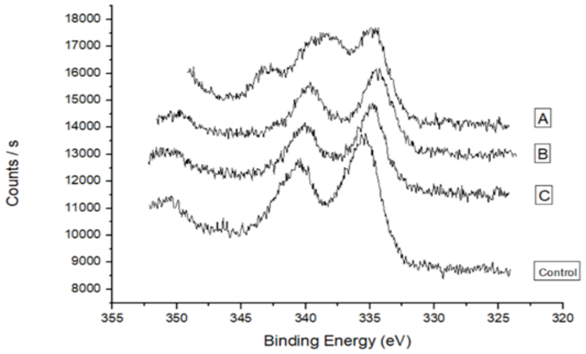

Figure 3. XPS characterization of catalyst surface: Pd3d

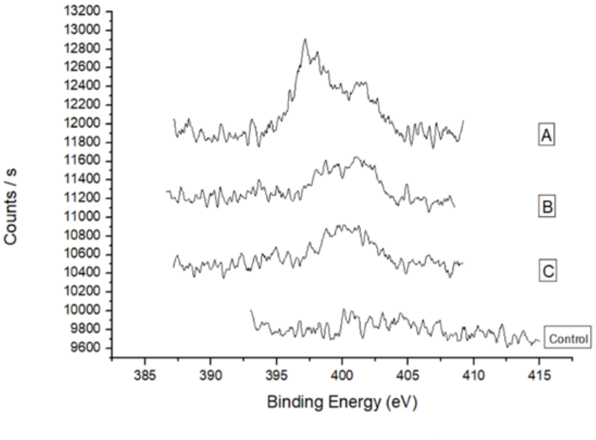

Figure 4. XPS characterization of catalyst surface: N1s

Table 1. The percentage of atoms of the main elements on the surface of the catalyst

Sample	Pd3d	C1s	N1s
A	1.33	14.11	2.51
B	1.23	7.23	1.32
C	1.32	8.50	1.15
Control	1.68	/	/

Note that ND means non-detectable (normally element percentage is below 0.1%)

71% in comparison of the control (5.3 m^2/g). The catalyst pore volume was reduced by nearly 10% after poisoning. Normally the specific surface area and pore volume have a linear correlation. However, the increase of the specific surface area in our plant-scale operation was observed along with a decrease of pore volume. The carrier of the catalyst is α-type alumina, which is a material with large pores and low specific surface area. Some substances may be generated during the ammonia-induced poisoning process, and it appears that they are likely to adsorb onto the surface of the inner pore of the carrier, which may result in a decrease in pore volume and the formation of "false surfaces," leading to an observation of the increase of the specific surface area. Combined with the analysis results, we speculate that some high-boiling amine compounds are formed after ammonia enters the reaction system. These substances are adsorbed on the pores and surface of the catalyst and increase the specific surface area of the catalyst. However, the catalyst activity is significantly affected by the binding of ammonia and amine substances with the active ingredient Pd.

3.4 Regeneration of Inactive Pd Catalysts

Based on the above-mentioned mechanism of ammonia poisoning, it can be assumed that the catalyst activity should be significantly restored if the amine compounds on the poisoned catalyst are effectively removed. In this case, the method of high-temperature roasting and further reduction can be adopted. Mu *et al.*[32] summarized the deactivation and reuse of DMO synthesis catalysts. Chemical plants usually use steam, acid washing, or alkaline washing to remove organic compounds on the catalyst surface at high temperatures. However, in industrial plants, the design temperature of the reactor generally does not exceed 200 °C,

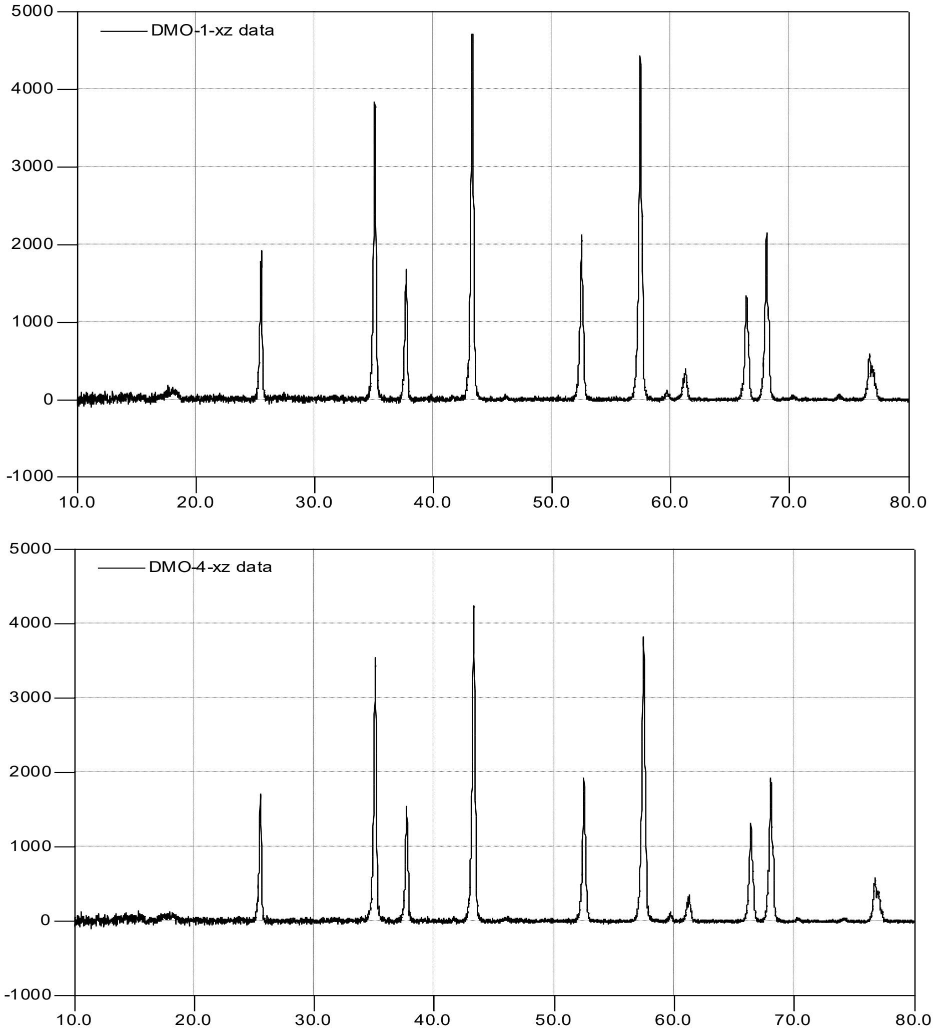

Figure 5. XRD characterization of catalyst surface: poisoning (top) and intact (bottom) catalyst samples

which makes it difficult to achieve in-situ regeneration in the reactor.

The low-temperature regeneration of the poisoned catalyst was carried out in liquid phase respectively. Sample I to IV were regenerated with formaldehyde, sodium hydroxide solution, ethyl acetate, methanol. Results are shown in Table 2. As shown in the Table 2, the catalyst activity was significantly restored after the regeneration treatment, especially sample IV (100% restored). Using the method associated with sample (IV) in December 2015, the catalyst used in the B-line with an annual output of 200,000 tons of ethylene glycol was regenerated. The regenerative plant was back to operation in March 2016. The regenerative B-line's performance is equivalent to the intact A-line. The regenerated catalyst's activity has been stable for more than 5 years and can continue to be used. Because low-temperature liquid phase regeneration can significantly restore catalyst activity, the catalyst's irreversible deactivation from ammonia poisoning is mainly caused by the formation of high boiling-point amine compounds that adsorb on the catalyst. Using liquid phase, organic solvent, and low-temperature regeneration, the Pd content does not change, because the process of treatment will not have a reaction associated with the catalyst active component Pd.

In comparison to other regeneration methods for ammonia-induced catalysts, our method shows advantages of regeneration efficiency/performance, low energy consumption, and the capability to achieve in-situ regeneration with a plant-scale treatment. The novelty of our method is to develop a low-temperature dissolving technology to remove the high-boiling nitrogen-containing compounds formed by reacting with ammonia.

4. Conclusion

The trace amount of ammonia (0.002%) in the feeding gas can cause significant poisoning and deactivation of the catalyst for DMO synthesis, which is not completely reversible. There are two reasons for the deactivation. One is that the competitive adsorption of ammonia molecules on Pd^{2+} hinders the CO coupling reaction and the redox cycle of active Pd on the surface of the catalyst. This type of deactivation can be restored after ammonia being removed. The other reason is that the adsorption of high-boiling amine compounds produced by the reaction on the catalyst retards the progress of the coupling reaction, which is irreversible. The low-temperature liquid phase regeneration can effectively remove the amine compounds adsorbed on the catalyst, leading to the catalyst activity being completely restored. The method has been applied to our industrial devices. Up to now, the service life of the regenerated catalyst has exceeded 5 years.

Acknowledgment

This work was financially supported by Hubei Science and Technology Development Project (P20501400001). Thanks to our partners, Wei-jian Chen, Guo-jian Zhang, Jian-yong Shuang, from Wuhuan Engineering Co., Ltd.

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Table 2. The STY of the catalyst after treating by different regeneration methods (I-IV)

Temperature (°C)	Sample (I)	Sample (II)	Sample (III)	Sample (IV)	Control	Poisoned
100	463	492	524	561	557	247
120	598	620	654	692	698	516

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