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Performance and Industrial Application of New-Type Sulfur Tolerant CO Shift Catalyst QDB-04

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Abstract

This paper presents the performance and characteristics of new-type sulfur tolerant shift catalyst QDB-04 and its industrial side-line test as well as the first-time industrial application in Lunan Chemical Fertilizer Plant of Shandong in China. The results show that the catalyst has high strength and strength stability, good low temperature activity and stability as well as low potassium bleeding ratio which well meet for the requirements of the methanol plant on catalyst performance in Lunan Chemical Fertilizer Plant.

Keywords

Sulfur Tolerant Shift Catalyst, Performance, Industrial Side-Line Test, Application

1. Introduction

Great attentions have been paid to the sulfur tolerant shift catalyst because of its excellent shift activity, sulfur tolerant ability and poisoning resistance. Many brands of such catalyst have been developed in the world, for example, K8-11 of BASF in Germany, SSK of TOPSOE in Denmark and QDB series of Qindao Lianxin Catalytic Materials Co., Ltd [1] [2]. The above catalysts have two kinds of supports, $MgAl_2O_4$ and γ-Al_2O_3. $MgAl_2O_4$-based catalyst has better strength and stability which can be applied in large-scale ammonia plant with high pressure, high water/gas ratio [3] [4]. But these kinds of catalysts have complicated production process and high price. So the γ-Al_2O_3-based catalyst is the first choice of small and medium-scale chemical fertilizer plant in China. The catalyst has simple production process, low price, high low-temperature activity, but its strength and

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strength stability are not good enough, especially when it gets powdered in operation which can cause the rise of bed resistance and affect the normal operation of the production. On the other hand, this kind of catalyst has other shortcomings such as high potassium bleeding rate, worse low sulfur resistance and easy deactivation caused by devulcanization [5].

In order to solve the above problems, we adopted a new catalyst production method and developed a new-type sulfur tolerant shift catalyst QDB-04 with special inorganic and organic assistants, using a special method of potassium fixation. The catalyst was first applied in the new industrial methanol device of Shandong Lunan Second Nitrogen Fertilizer Plant of China in June 2004. In December 2005, the catalyst passed the industrial application appraisal organized by Shandong Science and Technology Committee. The catalyst has excellent strength, strength stability and activity stability, good low-temperature activity, strong resistance to low water/gas ratio and low sulfur as well as low alkaline metal bleeding ratio which well satisfy the demand of sulphur containing feed gas and medium pressure shift process conditions on catalyst performance and its comprehensive performance reaches first-rate level in China.

This paper presents the performance, characteristics and first-time industrial application of the new-type sulfur tolerant shift catalyst QDB-04 in Lunan Chemical Fertilizer Plant of Shandong in China.

2. Methodology

2.1. Catalyst Preparation

Industrial catalysts of QDB-04 with special assistants were prepared by the dry-mixed method. The catalysts were extruded with special binder in order to get excellent strength performance.

2.2. Catalyst Activity Measurement

The intrinsic activity of the catalyst was tested in a atmospheric micro reactor chromatography evaluation apparatus, using CO conversion ratio (XCO, %) as catalytic activity expression. The composition of the feed gas was 44% CO, 25% CO, 0.005% - 0.05% H2S and remaining for H_2. The feed dry gas space velocity was 10,000 h^{-1}, water-gas ratio was 1.0, weight of samples was 0.3 grams, particle size of catalyst was from 0.25 to 0.35 millimeter. The reaction temperature was selected for 260˚C, 350˚C, 400˚C.

2.3. Catalyst Characterization

The active component of cobalt and molybdenum was determined by spectrophotometric method, and the content of potassium assistant was tested by flame photometric detector.

The strength was tested in the DL-II intelligent strength test instrument with average size as the evaluation means. The strength stability and potassium bleeding ratio were checked by hydro-thermal treatment experiment in the original size pressure evaluation device, the strength and potassium content of samples were determined after treatment for ten hours in atmosphere of nitrogen and stream with a pressure of 50 bar, a temperature of 500˚C, a space velocity of 2000 h^{-1} and a water-gas ratio of 1.4.

The XRD characterization was performed on the Rigaku D/Max - 1200 X-ray diffractometer, using Cu-Ka1 target, graphite monochromator, 50 kv voltage in X-ray tube, 100 Ma current. The specific surface area, pore structure were determined by the PM-60 mercury intrusion porosimeter.

3. Results and Discussion

3.1. Main Performance and Characteristics

3.1.1. Strength and Strength Stability

The experiment data are shown in **Table 1**. The QDB-04 had excellent strength and strength stability with special production process for its support. Whether fresh sample or the ones applied in industrial plant, the strength retention ratio of QDB-04 keeps well above 90% which shows very good strength stability.

3.1.2. Ability of Low Sulfur Tolerance

The ways of potassium assistant make a big influence on activity of sulfur tolerant shift catalysts [6]. With a special potassium fixation style, the “sulfur capture” ability of the catalyst can be improved by enhancing the

Table 1. Comparison of catalyst strength and stability.

Item	QDB-04		Industrial catalyst A	
	Strength, N/cm	Retention ratio	Strength N/(particle)	Retention ratio
Fresh catalyst	136.8	/	78.6	/
Catalyst after 1 year industrial used	131.9	96.4%	48.2	61.3%

sulfur on the surface of the catalyst, lowers the sulfur loss rate of the catalyst when the H_2S concentration is low in the feed gas [7] [8], and keeps relatively more activity center, so the catalyst activity is improved under low H_2S conditions, *i.e.*, the catalyst low sulfur tolerance is improved. The results are shown in **Table 2**.

Table 2 shows that when the H_2S content in the feed gas is above 0.05%, the two samples have almost the same catalytic activity; but with the lowering of the H_2S content, the sample with special potassium fixation style has obviously higher catalytic activity. This shows that the sample with special potassium fixation style has better low sulfur tolerance and higher activity under low H_2S conditions.

3.1.3. Potassium Bleeding Ratio

After hydro thermal treatment, different samples show different potassium bleeding ration. By a special potassium fixation style, the potassium-bleeding ratio of the catalyst under the same appraisal conditions can be decreased greatly with a result of high activity stability. The experiments show in **Table 3**.

3.1.4. Activity and Sulfurization Characterization

Table 4 shows the activity test result. It can be indicated that the special assistant helps the sample get better eigen activity under high sulfur and low sulfur conditions than the samples with no such special assistant. And the most likely reason from previous research is that special assistant promotes the reduction of Mo^{6+} with no activity to the active Mo^{4+} and improves the catalyst shift activity [9].

Table 5 shows the sulfurization performance of special assistant-promoted catalyst. Its sulfurization time has been shorted obviously. There was a theory from P Hou [9] may be as the explanation which is that the added special assistant changes the integration form between the active component and support which promotes the interchange reaction of S-O bond at low temperature.

3.2. Industrial Side-Line Test

On the whole low temperature shift industrial device of Shandong Lunan First Nitrogen Fertilizer Plant, 600 h and 1500 h industrial side-line test were carried out under the relative process conditions to the feed gas before and after deoxidation. The running data are shown in **Table 6** and **Table 7**.

It can be seen in **Table 6** and **Table 7** that:

1) Whether with oxygen-containing or deoxidized feed gas, QDB-04 always showed high shift activity; under running conditions similar to those of Lunan First Nitrogen Fertilizer Plant, the outlet CO of QDB-04 was 1.93 - 3.91 (for deoxidized feed gas) and 1.98 - 4.54 (for oxygen-containing feed gas) which was the process index of CO < 8% of the plant at the same period of time and showed that the catalyst activity can completely satisfy the process condition requirements of the same kind of plants.

2) In the course of the test, several times of startups and shutdown occurred due to the valve failure and pipe corrosion, but the catalytic activity and bed resistance drop remained almost the same which showed that the catalyst has quite good activity and strength stability.

3.3. Industrial Application Test

3.3.1. Industrial Operation Data

The domestically designed 100,000 t/a methanol device of Shandong Lunan Second Nitrogen Fertilizer Plant adjusts its shift furnace outlet CO index by adjusting the water/gas ratio. Its characteristics require the catalyst selected should have excellent ability to be tolerant of low water/gas ratio (0.3 - 0.4), relatively low activation temperature (240˚C) and good heat tolerance (heating point temperature 440˚C). For its first time operation, they chose our new-type sulfur tolerant shift catalyst QDB-04 (the diameter of the methanol shift furnace was 2.39 m,

Table 2. Relations between H_2S content in the feed gas and catalyst activity with different potassium fixation style.

	H_2S content in feed gas, %	0.05	0.03	0.02	0.01	0.005
CO shift ratio %	Sample with special potassium fixation	48.6	48.0	47.6	46.0	46.3
	Sample with common potassium fixation	48.2	41.2	37.8	35.2	32.4

Table 3. Potassium content and bleeding ratio of catalysts.

Sample	Fresh catalyst K_2O%	Hydrothermal treatment, K_2O%	Potassium bleeding raito, %
Special potassium fixation style	8.57	6.72	21.59
Common potassium fixation style	8.58	3.26	62.00

Table 4. Comparison of the catalyst activity under atmospheric pressure.

Catalyst	CO shift ratio, %			
	265˚C	350˚C	400˚C	
	H_2S > 500 ppm	H_2S > 500 ppm	H_2S > 500 ppm	H_2S, 160 ppm
Sample with special assistant	7.10	38.64	59.68	56.13
Sample without special assistant	6.32	33.38	54.51	48.98

Table 5. Comparison of catalyst sulfurization performance.

Catalyst	H_2S in the tail gas	
	Penetration time, h	Balance time, h
Sample with special assistant	4	12
Sample without special assistant	10	27

Table 6. Test data of the 1500 h industrial side-line test with deoxidized feed gas.

Time	Space velocity, h^{-1}	Temperature, ˚C			Tail gas, CO%	Shift ratio, %
		Top	Middle	Bottom		
2010.06.01	2000	201	245	203	5.24	79.06
2010.06.05	2000	202	252	203	5.21	79.18
2010.06.09	2000	221	264	221	4.60	81.51
2010.06.13	2000	248	270	245	4.32	82.59
2010.06.17	2000	240	270	240	4.90	80.35
2010.06.23	2000	240	285	252	5.02	79.90
2010.07.03	2000	235	240	240	4.58	81.58
2010.07.07	2000	240	260	240	4.75	80.93
2010.07.12	2500	245	260	240	4.70	81.12
2010.07.17	3500	240	280	245	5.87	76.69
2010.07.20	2500	235	240	245	5.46	78.23

the reaction system totally had 6 thermocouples which respectively indicated the temperature of inlet, upper bed, lower bed and outlet. Catalyst was loaded in a 6.4m^3 upper layer and a 6.6 m^3 lower layer). Industrial operation started from June, 2012 and has applied from then on. At the start of the operation, because the new device was put into operation for the first time, the bed temperature had risen to a high 838˚C. But we tried our best to control the temperature and the device soon reached full-load operation.

Table 7. Test data of the 600 h industrial side-line test with oxygen-containing feed gas.

Time	Space velocity, h^{-1}	Temperature, ˚C				Tail gas, CO%	Shift ratio, %
		Inlet	Top	Middle	Bottom		
2011.07.20	2500	216	298	278	245	2.97	87.87
2011.07.22	2500	217	304	293	263	3.06	87.51
2011.07.24	2500	224	318	300	269	3.83	84.49
2011.07.26	2500	225	318	296	273	3.38	86.25
2011.07.28	3000	223	324	332	301	4.05	83.63
2011.07.30	3000	223	344	346	323	4.01	83.79
2011.08.01	3000	224	307	352	336	6.81	73.19
2011.08.03	3000	224	304	349	332	5.91	76.53
2011.08.05	3000	225	306	355	338	5.33	78.72
2011.08.07	3000	221	309	359	338	5.15	79.40
2011.08.09	3000	222	318	362	341	4.47	82.01

Note: CO% in feed gas was 31.20%; Xco = (inlet CO%-outlet CO%)/[inlet CO% × (1 + outletr CO%)] × 100%.

Part of the industrial operation data of QDB-04 in Shandong Lunan Second Nitrogen Fertilizer Plant are shown in **Table 8**. It is seen from **Table 8**.

1) At the beginning of the startup with low operation load, the 216˚C - 225˚C inlet temperature was enough to satisfy the requirements for CO outlet content (20% - 23%) in the methanol device which showed that the QDB-04 catalyst has good low temperature activity.

2) Due to the serious overheating of the QDB-04 catalyst at the beginning of the startup and several times of startups and shutdowns in the operation, the inlet temperature was improved about 10˚C (from 255˚C to 266˚C at full load) in the latter period of operation. In spite of this, the catalyst can still satisfy the requirements of the methanol device which shows the good activity and structure stability of QDB-04.

3) During the operation, the bed resistance drop maintained almost the same which showed that there're no powdering and crushing of the catalyst in the course of operation and it keeps good strength and strength stability.

4) In the course of the new device running, there're frequent startups and shutdowns and frequent changes of load, pressure, water/gas ratio, but QDB-04 catalyst still maintained stable performance and it showed resistance to operating condition fluctuations.

3.4. Sample Analysis of the Industrially Used Catalyst

3.4.1. Exterior

During the overhaul of Lunan Chemical Fertilizer Plant in March, 2012, part of the upper layer catalyst in the shift furnace was replaced because there was an overheating to 838˚C of the upper layer catalyst which might affect the long time production. After comparing the upper and lower layer samples, it was found that QDB-04 catalyst remained its whole particle with no caking and powdering, albeit the upper layer overheated sample got a paler color.

3.4.2. Strength

Comparison of the strength between the fresh sample and used sample is listed in **Table 9**. **Table 9** shows that QDB-04 catalyst retained 98% of its strength in both the upper and lower part of the furnace after one year's operation. The overheated samples still retained 85% of its strength.

3.4.3. Bleeding of the Active Components

Contents of alkaline metal K_2O and active component MoO_3 are examined for the samples from upper and lower parts of the upper layer after one year industrial operation (see **Table 10**). The data show that their alkaline metal

Table 8. Part of the operation data of QDB-04.

Date	Gas flowrate	Temperature, ˚C							
	N m^3/h	Inlet	First layer		Second layer		Outlet	Outlet	Resistance drop
2012.06.04	5251	216	399	401	438	429	432	23.21	6
2012.06.10	8303	225	414	418	428	422	424	23.17	8
2012.06.25	10764	221	405	412	418	415	408	18.64	10
2012.07.15	12900	218	399	408	413	414	419	21.95	12
2012.08.01	27871	242	325	398	432	424	430	21.38	30
2012.09.25	30814	255	329	395	425	413	421	20.31	30
2012.10.10	32025	254	335	402	428	420	420	22.8	30
2012.10.25	27885	252	326	393	430	417	427	20.9	30
2012.11.30	24123	244	404	436	440	439	436	22.53	23
2012.12.16	33977	246	318	380	427	404	424	21.67	30
2013.01.07	33100	259	351	414	435	426	430	21.45	30
2013.01.21	33490	266	339	403	432	418	428	22.74	30
2013.02.27	33753	264	357	418	433	440	436	22.35	31
2013.03.31	28962	230	348	417	428	428	427	20.2	30
2013.04.21	33285	234	351	410	419	419	418	19.74	30
2013.05.15	33860	236	349	415	424	425	424	21.32	31

Table 9. Strength comparison of QDB-04 catalyst samples before and after industrial operation.

Catalyst		Strength, N/cm	Retention ratio, %
Fresh sample		137.8	/
After one	Upper part of the upper layer	135.4	98.3
Year's operation	Lower part of the upper layer	118.4	85.9
	Middle part of the lower layer	136.9	99.3

Table 10. Comparison of the active component of QDB-04 catalyst samples before and after industrial operation.

Catalyst		MoO_3 content,	K_2O, %
Fresh sample		7.49	8.23
After one	Upper part of the upper layer	7.36	8.24
Year's operation	Lower part of the upper layer	6.76	8.18

content remains the same to that of the fresh sample after one year's operation, so are the MoO_3 and K_2O content from the upper layer, but the sample from overheated part shows paler color, and its MoO_3 content is 6.76% which is obviously lower than that of the upper layer sample because of the sublimation of the active component during the period of overheating at over 800˚C [10].

3.4.4. Phase Composition and Pore Structure

Table 11 shows the comparison of the XRD phase composition and pore structure of QDB-04 catalyst between samples after one year's industrial operation and the fresh sample. It is shown from **Table 11** that specific area of the catalyst from different sites of the furnace was all reduced a little, especially the sample from the lower part of the upper layer. There are also bigger pore distribution changes in the lower part samples from the upper

Table 11. Comparison of the physi-chemical performance of QDB-04 catalyst before and after industrial operation.

Item	Fresh sample	After one year industrial operation		
		Upper part of upper layer lower layer	Lower part of upper layer	Middle part of
Specific area	115.1	105.2	92.7	99.4
Pore volume	0.3609	0.2832	0.2953	0.3283
Average pore radius, nm	62.81	59.50	63.63	59.99
Most probable radius, nm	3.16	2.756	3.035	2.941
Pore distribution				
<25 nm	57.47	57.79	57.31	56.48
25 - 50 nm	5.11	6.05	7.28	5.91
50 - 150 nm	13.95	20.38	22.61	27.11
>150 nm	23.39	15.79	12.79	10.51
XRD phase composition	γ-Al_2O_3	γ-Al_2O_3	γ-Al_2O_3	γ-Al_2O_3
	$MgAl_2O_4$	$MgAl_2O_4$	$MgAl_2O_4$	$MgAl_2O_4$
		K_2SO_4 (micro amount)		

layer, among which small pores (<25 nm) remain almost the same but 50 - 150 nm medium-size pores are increased and big pores (>150 nm) are reduced obviously. The specific surface and pore structure changes are all caused by the serious overheating at the beginning of the startup.

It is also seen from **Table 11** that even for the sample from the overheated part, its specific area was only decreased by 23.9% and other physical properties change relatively small. This shows that QDB-04 catalyst not only has good activity stability but also has good structure stability.

Table 11 also lists the phase data of QDB-04 before and after industrial application. It is shown that after one year's operation, the physical composition remains almost the same except the micro K_2SO_4 engendering in the upper part which further indicates the good structure stability of the catalyst.

4. Conclusions

1) Experiment tests show that QDB-04 is a sulfur tolerant CO shift catalyst with special support and new-type assistant which have the properties of high strength and strength stability, high resistance to powdering, good low-temperature activity and activity stability, low alkaline metal bleeding ratio and easy sulfurization.

2) Industrial application results show that QDB-04 catalyst has low activation temperature, high low-temperature activity, high activity stability and high resistance to low water/gas ratio, which can perfectly satisfy the requirements of the methanol device of Lunan Nitrogen Fertilizer Plant. It overcomes the shortcomings (such as peeling and powdering that cause the rise of bed resistance) of the γ-Al2O3-based industrial catalyst.

3) Analysis of the unloaded sample shows that QDB-04 catalyst stands the one-year industrial operation and serious over-heating accident and retains the original bed resistance and catalysis activity. The unloaded samples keep high retention ratios of strength, pore structure and active component which show its good strength, strength stability and corrosion resistance. It can satisfy the requirements of methanol process conditions to catalyst activity, strength and structure stability.

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