Al₂O₃ 性质对加氢脱硫催化剂 Co-Mo/Al₂O₃ 活性相形成的影响

齐和日玛^{1,3}, 李会峰², 袁 蕙², 张韞宏¹, 徐广通²

¹ 北京理工大学化学物理研究所, 北京 100081

² 中国石化石油化工科学研究院, 北京 100083

³ 内蒙古医学院药学院, 内蒙古呼和浩特 010059

摘要: 以两种商用 Al₂O₃ 为载体, 制备了汽油选择性加氢脱硫催化剂 Co-Mo/Al₂O₃, 并采用红外光谱、X 射线衍射、N₂ 吸附-脱附、透射电镜、扫描透射-能谱和 X 射线光电子能谱等手段系统研究了载体物化性质对催化剂活性相形成的影响。结果表明, 表面羟基数量少和结晶程度高的载体与活性金属间相互作用减弱, 促进了 Mo 物种的硫化还原, 使 MoS₂ 片晶的尺寸和层数增加, 且其硫化态催化剂上 CoMoS 活性位更多, CoMoS/MoS₂ 比更大, 因而显著提高了相应 Co-Mo 催化剂加氢脱硫活性和选择性。

关键词: 氧化铝; 物化性质; 钴; 钼; 加氢脱硫; 活性相

中图分类号: O643

文献标识码: A

Effect of Alumina Supports on the Formation of Active Phase of Selective Hydrodesulfurization Catalysts Co-Mo/Al₂O₃

Qiherima^{1,3}, LI Huifeng², YUAN Hui², ZHANG Yunhong¹, XU Guangtong^{2,*}

¹The Institute for Chemical Physics, Beijing Institute of Technology, Beijing 100081, China

²Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China

³Department of Pharmacy, Inner Mongolia Medical College, Hohhot 010059, Inner Mongolia, China

Abstract: Two different commercial alumina supports were used for the preparation of selective hydrodesulfurization (HDS) catalysts Co-Mo/Al₂O₃. The effect of support properties on the HDS activity and selectivity of the corresponding Co-Mo catalysts were studied by X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, scanning transmission electron microscopy-energy dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. The HDS activity and selectivity were measured using a continuous flow fixed-bed microreactor. The Al₂O₃ support with higher crystallinity and fewer hydroxyl groups had a moderate metal-support interaction, which resulted in an increase of the average slab length and stacking number of MoS₂. This gave more formation of the active CoMoS phase and an increase in HDS activity and selectivity.

Key words: alumina; property; cobalt; molybdenum; hydrodesulfurization; active phase

Al₂O₃ 具有适宜的比表面积和孔径分布、良好的机械强度和稳定性等良好特性, 且铝土资源较为丰富, 因而被广泛用作催化剂载体。炼油工业中所用的加氢处理催化剂 (除加氢裂化催化剂外) 几乎都采用 Al₂O₃ 为载体的主要成分^[1]。然而 Al₂O₃ 的物化性质对负载型催化剂性能影响很大^[2~7]。Domínguez-Crespo 等^[5]研究了 Al₂O₃ 晶粒大小对 Ni-Mo/

Al₂O₃ 催化剂加氢脱硫 (HDS)、加氢脱氮 (HDN) 和加氢脱芳烃 (HDA) 活性的影响。Sakashita 等^[6,7]报道了 Al₂O₃ 晶面取向和结晶度与硫化态 Mo/Al₂O₃ 催化剂微观结构的关系, 并指出通过调整 Al₂O₃ 载体晶面取向可控制 MoS₂ 簇的微结构。但由于能够用于直接测试 HDS 催化剂硫化态活性相的表征手段有限, 有关载体的物化性质对催化剂活性相及选

收稿日期: 2010-09-21. 接收日期: 2010-10-21.

联系人: 徐广通. Tel/Fax: (010)82368613; E-mail: gtxu@sina.com

基金来源: 国家重点基础研究发展计划 (973 计划, 2006CB202506), 国家科技支撑计划 (2007BAE43B01); 石油化工催化材料与反应工程国家重点实验室 2009 年开放课题。

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).

择性影响的报道较少.

为了开发高选择性的 HDS 催化剂, 本文以两种商用 Al_2O_3 为载体, 制备了 Co-Mo/ Al_2O_3 催化剂, 采用红外光谱 (FT-IR)、X 射线衍射 (XRD)、 N_2 吸附-脱附、透射电子显微镜 (TEM)、扫描透射-能谱 (STEM-EDX)、X 射线光电子能谱 (XPS) 和低温 CO 吸附 FT-IR 等手段, 研究了 Al_2O_3 载体的物化性质与 Co-Mo/ Al_2O_3 的活性相及其 HDS 活性和选择性的关系.

1 实验部分

1.1 催化剂的制备

以中国石化长岭催化剂厂生产的两种商用 Al_2O_3 (命名为 Al_2O_3 -1 和 Al_2O_3 -2) 为载体, 将一定量的硝酸钴和钼酸铵溶于氨水溶液中, 定容配制成共浸液, 在室温浸渍氧化铝载体 2 h, 然后于 393 K 干燥 2 h, 在流动空气气氛下于 693 K 焙烧 4 h. 得到的催化剂样品分别记为 Co-Mo/ Al_2O_3 -1 和 Co-Mo/ Al_2O_3 -2, 其中 MoO_3 和 CoO 的负载量均分别为 8.0% 和 2.5%.

1.2 载体和催化剂的表征

载体的表面性质表征在 Nicolet 6700 型 FT-IR 红外光谱仪上进行, 分辨率 4 cm^{-1} , 扫描次数 64 次. 首先将载体磨成细粉, 然后压制成自撑片置于原位池中密封, 升温至 673 K 抽真空保持 4 h. 待温度降至 373 K 时采集谱图. 之后, 向原位池中通入吡啶蒸气, 维持吸附平衡 15 min 至饱和, 将体系升温至 473 K 真空脱附 30 min 后降至 373 K, 采集样品 FT-IR 谱. 然后将体系升至 623 K 真空脱附 30 min 后降温至 373 K, 采集样品谱图.

采用美国康塔公司 Autosorb-6B 型物理吸附仪测定样品的比表面积和孔体积.

样品晶相采用 Philips 公司 XPERT 型 X 射线衍射仪测定, Cu 靶 ($\lambda = 0.15418\text{ nm}$), 功率 35 kW, 电压 40 kV, 电流 50 mA, 扫描范围 $2\theta = 5^\circ \sim 80^\circ$, 步长 $0.02^\circ/\text{s}$.

采用 FEI 公司 Tecnai G² F20 S-TWIN 型透射电子显微镜表征样品形貌, 加速电压 200 kV, 配置 STEM 功能配件和 EDX 能谱系统. 样品超声分散于环己烷中. 硫化态催化剂片晶的尺寸分布通过统计约 500 个以上 MoS_2 片晶的几何参数计算得到.

MoS_2 片晶的平均长度 ($\bar{L}$)、平均堆叠层数 ($\bar{N}$) 和 1000 nm^2 观测面积上的 MoS_2 片晶的平均个数 ($\bar{D}$) 根据以下公式计算得到^[8]:

$$\begin{aligned}\bar{L} &= \sum_{i=1}^n n_i l_i / \sum_{i=1}^n n_i \\ \bar{N} &= \sum_{i=1}^n n_i N_i / \sum_{i=1}^n n_i \\ \bar{D} &= (n/S) \times 1000\end{aligned}$$

用 STEM-EDX 对焙烧后氧化态催化剂上活性组分 Co 和 Mo 进行微区元素分布分析, 样品制备方法同 TEM.

低温 CO 吸附的 FT-IR 谱在 Bruker 公司 EQUINOX 55 型 FT-IR 红外光谱仪上测定. 将氧化态催化剂样品压成自支撑片, 放入自制低温红外石英样品池. 先以 10% H_2S -90% H_2 混合气体在 673 K 将样品硫化 5 h, 然后密封降至室温. 再与高真空系统连接, 边抽空边将样品升温到 573 K, 并保持 3 h. 然后让样品自然降到室温, 在样品池冷却夹套中注入液氮, 使样品降温至约 100 K. 导入 CO 在常压下饱和和吸附约 30 min, 抽去气相 CO. 通过摄取样品吸附 CO 前后差谱得其吸附 CO 的 FT-IR 谱. 实验使用的 CO 经过液氮冷凝净化处理.

在 Ar 保护下, 将 CO 吸附 FT-IR 谱测试后的样品从密封的原位池迅速转移到 Thermo Scientific 公司 ESCALab250 型 XPS 装置分析室中. 激发源为单色化功率为 150 W 的 $\text{Al K}\alpha$ X 射线, 荷电效应来自载体 Al_2O_3 的 Al 2p 峰 (74.7 eV) 校正. 谱峰拟合时, S 2p 和 Mo 3d 的自旋分裂间距分别设定为理论值 1.15~1.18 和 3.15~3.20; 峰面积比取理论值, 分别为 2.0 和 1.5; 自旋分裂峰如 Mo 3d_{5/2} 和 Mo 3d_{3/2} 的半高宽取相同值.

1.3 催化剂的评价

反应前用含 6 vol% CS_2 的环己烷溶液于 1.6 MPa, 593 K 对催化剂预硫化 3 h. 在固定床连续流动微反装置上, 以含 10% 噻吩和 20% 1-己烯的正庚烷溶液为反应油, 进行 HDS 反应, 催化剂装填量 1.00 g. 反应条件为: 1.6 MPa, 533 K, 进料速度 0.16 ml/min, H_2 流速 360 ml/min. 反应达稳态后, 自动取样, 在 Agilent 公司 6890 型气相色谱仪上进行在线分析. 按下式计算出催化剂的 HDS 活性 (X_T)、烯烃饱和 (HYD) 活性 (X_H) 及 HDS 选择性因子 (S)^[9]: $X_T = [(w_{T,1} - w_{T,2})/w_{T,1}]$, $X_H = [(w_{H,1} - w_{H,2})/w_{H,1}]$, $S =$

$\ln(1-X_T)/\ln(1-X_H)$. 其中 $w_{T,1}$ 和 $w_{T,2}$ 分别表示反应物和产物中噻吩的质量分数, $w_{H,1}$ 和 $w_{H,2}$ 分别表示反应物和产物中 1-己烯的质量分数.

2 结果与讨论

2.1 载体羟基、酸中心分布及其对表面金属分散性的影响

图 1(a) 为两种 Al_2O_3 载体的 FT-IR 谱. 可以看出, Al_2O_3 -2 样品表面羟基数量明显少于 Al_2O_3 -1. 载体上羟基的数量可能会影响负载金属组分的分散, 因为活性金属组分在载体上沉积后会减少载体羟基的数量, 表明羟基参与了活性金属与载体间的相互作用^[10]. 因此, 羟基较少的载体 Al_2O_3 -2 与金属组分间的相互作用减弱, 更有利于负载于其上的活性金属组分的硫化还原和硫化态活性相的形成. 图 1(b) 为两种载体在 473 和 623 K 吸附吡啶的 FT-IR 谱, 两个温度下 Al_2O_3 的酸量见表 1. 两种载体均无明显的 B 酸中心, 而对于 L 酸中心, Al_2O_3 -2 上相对较少. 这表明该载体接受电子的空位较少, 可导致载体与金属组分的相互作用较弱.

为了考察载体性质对负载于其上的活性金属分散度的影响, 本文采用 STEM-EDX 技术观察了 Co 和 Mo 组分在载体表面的分散状态, 结果见图 2. 可以看出, 活性金属在 Al_2O_3 -1 上的分布状态比在 Al_2O_3 -2 上更均匀.

图 1 两种 Al_2O_3 载体及其吸附吡啶的 FT-IR 谱

Fig. 1. FT-IR spectra of two Al_2O_3 supports (a) and pyridine adsorbed on the two Al_2O_3 supports at different adsorption temperatures. (a): (1) Al_2O_3 -1; (2) Al_2O_3 -2. (b): (1) Al_2O_3 -1, 473 K; (2) Al_2O_3 -2, 473 K; (3) Al_2O_3 -1, 623 K; (4) Al_2O_3 -2, 623 K.

表 1 两种 Al_2O_3 载体表面的酸含量

Table 1 Surface acid amounts of the two Al_2O_3 supports

Sample*	$C(\text{Lewis acid})/(\mu\text{mol/g})$		$C(\text{Brönsted acid})/(\mu\text{mol/g})$	
	473 K	623 K	473 K	623 K
Al_2O_3 -1	11.0	8.2	0	0
Al_2O_3 -2	7.4	5.8	0	0

*Two species of commercial alumina obtained from Changling Division of SINOPEC Catalyst Company.

图 2 氧化态催化剂 $\text{Co-Mo/Al}_2\text{O}_3$ -1 和 $\text{Co-Mo/Al}_2\text{O}_3$ -2 的 Co 和 Mo 元素的 STEM 面分布图

Fig. 2. Elemental mapping of Co and Mo in oxide catalysts $\text{Co-Mo/Al}_2\text{O}_3$ -1 (a and b) and $\text{Co-Mo/Al}_2\text{O}_3$ -2 (c and d). Red shows Mo, blue shows Co, and a lighter color shows a lower content of the element.

2.2 载体和催化剂的组织性质和物相

Al₂O₃ 载体和催化剂的组织性质见表 2。由表可见, Al₂O₃-1 和 Co-Mo/Al₂O₃-1 的比表面积和孔体积分别大于 Al₂O₃-2 和 Co-Mo/Al₂O₃-2 的相应值, 且催化剂比表面积和孔体积均接近于其相应载体。

表 2 Al ₂ O ₃ 载体和 Co-Mo/Al ₂ O ₃ 催化剂的组织性质		
Table 2 BET surface area and pore volume of the samples		
Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)
Al ₂ O ₃ -1	187	0.61
Al ₂ O ₃ -2	124	0.56
Co-Mo/Al ₂ O ₃ -1	174	0.53
Co-Mo/Al ₂ O ₃ -2	122	0.47

图 3 为各载体及其催化剂的 XRD 谱。可以看出, 两种载体均为 γ -Al₂O₃ 相 (PDF 48-367)。但 Al₂O₃-2 的衍射峰更尖锐, 强度更高, 说明 Al₂O₃-2 载体结晶度更高。从图 3 还可以看出, 金属 Co 和 Mo 的负载并没有明显改变相应载体的晶相, 但 Co-Mo/Al₂O₃-2 样品于 $2\theta = 26.5^\circ$ 处出现 β -CoMoO₄ 的特征衍射峰 (PDF 21-868), 表明该样品中 Co 和 Mo 较易发生相互作用。这可能与 Co-Mo/Al₂O₃-2 催化剂中 Al₂O₃-2 载体的结晶度高, 羟基量较少, 活性组分与载体作用弱有关。

2.3 硫化态催化剂的活性相分布特征

为了研究载体对催化剂活性相特征的影响, 对各硫化态催化剂进行了 TEM 表征, 结果见图 4。由图可见, 各催化剂 MoS₂ 活性相呈典型层状堆垛结构, 但两个样品中活性相的堆垛层数、长度和分散度均有明显差异。表 3 为各催化剂样品 MoS₂ 片晶平

图 3 Al₂O₃ 载体和 Co-Mo/Al₂O₃ 氧化态催化剂的 XRD 谱
Fig. 3. XRD patterns of two supports and oxide catalysts. (1) Al₂O₃-1; (2) Co-Mo/Al₂O₃-1; (3) Al₂O₃-2; (4) Co-Mo/Al₂O₃-2.

均长度、堆叠层数和分散度。可以看出, 与 Co-Mo/Al₂O₃-1 相比, Co-Mo/Al₂O₃-2 的 MoS₂ 片晶长度较大, 且片晶层数也较高, 这也说明 Co-Mo/Al₂O₃-2 中金属与载体间相互作用较 Co-Mo/Al₂O₃-1 弱。研究表明^[6], 硫化度与堆垛层数较高的 MoS₂ 片晶减弱了 Al₂O₃ 中 Al³⁺ 的极化作用, 促进了 Co 对 Mo 的助剂化作用, 有利于生成高活性的 CoMoS 活性相。

表 3 硫化态催化剂的活性相特征统计			
Table 3 Slab length, stacking number, and slab number of the sulfided Co-Mo/Al ₂ O ₃ catalysts			
Sample	Average slab length (nm)	Average stacking number	Slab number (1/(1000 nm ²))
Co-Mo/Al ₂ O ₃ -1	4.2	1.6	12.6
Co-Mo/Al ₂ O ₃ -2	5.6	2.3	8.7

图 4 硫化态催化剂的 TEM 照片
Fig. 4. TEM images of the sulfided catalysts. (a) Co-Mo/Al₂O₃-1; (b) Co-Mo/Al₂O₃-2.

2.4 硫化态催化剂的 XPS 结果

各硫化态催化剂样品的 Mo 3d 和 S 2p XPS 谱见图 5. 表 4 为不同化学态 Mo 和 S 的结合能, 与文献报道值吻合^[11,12]. Mo 3d 在 228.8 和 232.0 eV 显示出强双重带, 归属于 $\text{Mo}^{4+} 3d_{5/2}$ 和 $\text{Mo}^{4+} 3d_{3/2}$ 的特征结合能, 表明 Mo 主要以 Mo^{4+} 的形式存在. 在 232.4 和 235.8 eV 处较弱的谱峰是未硫化的 Mo^{6+} 物种, 230.3 和 233.6 eV 处的峰则是 O-Mo-S 相中的 Mo^{5+} 物种, S 2s 的峰位与 $\text{Mo}^{4+} 3d_{5/2}$ 较近, 谱峰有一定的重叠, 定量分析时要除去其影响. 161.7 和 163.0 eV 附近呈现出 S^{2-} 的特征峰, 可归属于 MoS_2 相中端基 S^{2-} 或 S^{2-} 配体, 163.6 和 164.7 eV 处峰对应于桥基 S_2^{2-} 或氧硫形式存在的 S 物种, 与 Mo^{5+} 物种结合生成氧硫化物 MoO_xS_y . 在 169.0 eV 处没有观察到 S 物种的信号, 表明硫化态催化剂没有发生氧化现象. 由表 4 可见, 两种催化剂中各物种结合能基本一致, 表明所研究的载体物化性质对主要物种化学态的影响不大, 但对不同化学态物种间比值有一定影响.

根据 XPS 谱图的分峰拟合结果, 计算催化剂中各物种不同化学态的比值, 结果见表 4. Mo 物种的

硫化度用 $n(\text{Mo}^{4+})/n(\text{Mo})$ 比值来进行推算. 由表 4 可见, Co-Mo/ Al_2O_3 -2 中 $n(\text{Mo}^{4+})/n(\text{Mo})$ 比值高于 Co-Mo/ Al_2O_3 -1, 说明 Co-Mo/ Al_2O_3 -2 中 Mo 的硫化度更高, 其中 Mo^{6+} 物种在总 Mo 物种中所占比例 $n(\text{Mo}^{6+})/n(\text{Mo})$ 明显少于 Co-Mo/ Al_2O_3 -1, 可见难硫化的 Mo 物种在 Co-Mo/ Al_2O_3 -2 中较少, Co-Mo/ Al_2O_3 -2 中载体与活性金属的相互作用较弱, 这与 FT-IR 和 TEM 结果一致. 需要说明的是, 由于 Co 2p 的 XPS 信号很弱, 本文未对 Co 2p 进行分峰拟合. 表 4 只给出了总 Co 在载体上的分散数据 ($n(\text{Co})/n(\text{Al})$), 可以看出, Co-Mo/ Al_2O_3 -2 中 Co 在载体上的分散度比 Co-Mo/ Al_2O_3 -1 高.

2.5 硫化态催化剂活性相的 CO 探针吸附原位 FT-IR 结果

低温下 (~100 K) CO 作为一个供电子的探针分子可吸附在硫化态 CoMo 催化剂不同形态的活性相上, 从而可通过 CO 的 FT-IR 研究不同化学态活性相的分布及其对催化剂性能的影响. 图 6 为两个催化剂吸附 CO 后的 FT-IR 谱. 2191 cm^{-1} 为与载体 L 酸中心 (Al^{3+}) 结合的 CO 吸收峰; 2153 cm^{-1} 是与载体弱酸性 OH 中心氢键结合的 CO 吸收峰. 2108

图 5 硫化态催化剂的 Mo 3d (a) 和 S 2p (b) XPS 谱

Fig. 5. Mo 3d (a) and S 2p (b) XPS spectra of the sulfided catalysts. (1) Co-Mo/ Al_2O_3 -1; (2) Co-Mo/ Al_2O_3 -2.

表 4 硫化态 Co-Mo/ Al_2O_3 催化剂中不同物种的结合能和定量分析结果

Table 4 Binding energy and quantitative results for different species of the sulfided Co-Mo/ Al_2O_3 catalysts

Sample	Binding energy (eV)					$n(\text{Mo}^{4+})/$ $n(\text{Mo})$	$N(\text{Mo}^{5+})/$ $n(\text{Mo})$	$n(\text{Mo}^{6+})/$ $n(\text{Mo})$	$n(\text{Co})/$ $n(\text{Al})$
	$\text{Mo}^{4+} 3d_{5/2}$	$\text{Mo}^{5+} 3d_{5/2}$	$\text{Mo}^{6+} 3d_{5/2}$	$\text{S}^{2-}/\text{terminal S}_2^{2-}$	$\text{S}_2^{2-}/\text{oxy-sulfide S}$				
Co-Mo/ Al_2O_3 -1	228.8	230.3	232.4	161.7	163.6	72.0	11.6	16.4	1.3
Co-Mo/ Al_2O_3 -2	229.0	230.5	232.8	161.9	163.4	77.7	12.5	9.8	1.6

图6 硫化态催化剂的低温吸附CO的FT-IR谱

Fig. 6. FT-IR spectra of CO adsorbed on the sulfided catalysts. (1) Co-Mo/ Al_2O_3 -1; (2) Co-Mo/ Al_2O_3 -2.

cm^{-1} 处谱峰归属于与六配位无助剂作用的Mo中心结合的CO峰,即 MoS_2 的配位不饱和位上吸附的CO峰;2069和 2051 cm^{-1} 谱峰归属于有助剂作用的活性中心上吸附的CO峰,分别是与CO作用的五配位和四配位且与Co相邻的Mo中心,即CoMoS活性中心上吸附的CO吸收峰^[13].

为了研究载体对各活性中心的影响,对谱图进行了分峰拟合.根据CO与催化剂中各中心的作用情况以及拟合需要,将谱图分解为 Al^{3+} ,OH, MoS_2 和三个CoMoS以及物理吸附等组分^[14,15],各峰的形状选择高斯分布,分峰示例见图6.吸附在CoMoS中心的CO(CO-CoMoS)的总强度为谱图分解后三个CoMoS上吸附的CO谱峰强度之和.CO-CoMoS和CO- MoS_2 峰的积分面积比值 $A(\text{CO-CoMoS})/A(\text{CO-MoS}_2)$ 可反映硫化态催化剂的助剂化作用程度.结果表明,Co-Mo/ Al_2O_3 -2的CO-CoMoS积分面积为6.2,高于Co-Mo/ Al_2O_3 -1的5.6,且Co-Mo/ Al_2O_3 -2的 $A(\text{CO-CoMoS})/A(\text{CO-MoS}_2)$ 比值8.33也远高于Co-Mo/ Al_2O_3 -1的4.03,表明Co-Mo/ Al_2O_3 -2样品中高活性CoMoS相的数量及其助剂化作用程度均高于Co-Mo/ Al_2O_3 -1,这将有助于提高催化剂HDS活性和选择性.

2.6 催化剂的HDS性能

各催化剂HDS活性和选择性见表5.可以看出,Co-Mo/ Al_2O_3 -2催化剂HDS活性明显高于Co-Mo/ Al_2O_3 -1,但两者烯烃饱和度基本相同,由各催化剂HDS选择性因子可知,Co-Mo/ Al_2O_3 -2催化

表5 两种催化剂的HDS活性和选择性

Table 5 Evaluation of HDS activity and selectivity of Co-Mo/ Al_2O_3 -1 and Co-Mo/ Al_2O_3 -2 catalysts

Catalyst	$X_T/\%$	$X_H/\%$	S
Co-Mo/ Al_2O_3 -1	30.9	58.2	0.4
Co-Mo/ Al_2O_3 -2	42.2	59.1	0.6

剂HDS选择性更高.结合上述表征结果可以认为,载体结晶度高,表面羟基和L酸中心数量少,与金属组分间的相互作用弱,有利于更多的易硫化还原的Mo物种生成;硫化度和堆垛层数较高的 MoS_2 片晶可以减弱 Al_2O_3 中 Al^{3+} 的极化作用^[16,17],促进Co对Mo的助剂化作用,生成更多的CoMoS相,因而有利于提高催化剂的HDS活性和选择性.

3 结论

采用多种分析手段表征了两种商用 Al_2O_3 载体及其负载的Co-Mo催化剂,并评价了催化剂的HDS活性和选择性.活性金属与结晶度高、表面羟基和L酸中心数量较少的载体 Al_2O_3 -2间相互作用较弱,更易硫化还原,且硫化度更高.同时,其相应Co-Mo催化剂上的 MoS_2 片晶尺寸更长,层数更高.另外,该催化剂的CoMoS活性相位的数量和 $A(\text{CO-CoMoS})/A(\text{CO-MoS}_2)$ 比均高于Co-Mo/ Al_2O_3 -1.因此Co-Mo/ Al_2O_3 -2催化剂上HDS活性和选择性也更高.

参 考 文 献

- 李大东.加氢处理工艺与工程.北京:中国石化出版社(Li D D. Hydrotreating Process and Engineering. Beijing: China Petrochemical Press), 2004. 181
- Meephoka C, Chaisuk C, Samparnpiboon P, Praserttham P. *Catal Comm*, 2008, **9**: 546
- He S B, Sun C L, Bai Z W, Dai X H, Wang B. *Appl Catal A*, 2009, **356**: 88
- Domínguez-Crespo M A, Torres-Huerta A M, Díaz-García L, Arce-Estrada E M, Ramírez-Meneses E. *Fuel Process Technol*, 2008, **89**: 788
- Domínguez-Crespo M A, Arce-Estrada E M, Torres-Huerta A M, Díaz-García L, de la Paz C M T. *Mater Charact*, 2007, **58**: 864
- Sakashita Y. *Surf Sci*, 2001, **489**: 45
- Sakashita Y, Araki Y, Shimada H. *Appl Catal A*, 2001, **215**: 101
- 左东华, 聂红, Michel V, 石亚华, Michel L, 李大东. 催化学报 (Zuo D H, Nie H, Michel V, Shi Y H, Michel L, Li

- D D. *Chin J Catal*, 2004, **25**: 309
- 9 Li M F, Li H F, Jiang F, Chu Y, Nie H. *Catal Today*, 2010, **149**: 35
 - 10 Zepeda T A, Pawelec B, Fierro J L G, Halachev T. *J Catal*, 2006, **242**: 254
 - 11 Gandubert A D, Krebs E, Legens C, Costa D, Guillaume D, Raybaud P. *Catal Today*, 2008, **130**: 149
 - 12 Qiu L M, Xu G T. *Appl Surf Sci*, 2010, **256**: 3413
 - 13 Travert A, Dujardin C, Mauge F, Veilly E, Cristol S, Paul J F, Payen E. *J Phys Chem B*, 2006, **110**: 1261
 - 14 陈文斌. [博士学位论文]. 北京: 中国石油化工股份有限公司石油化工科学研究院 (Chen W B. [PhD Dissertation]. Beijing: Research Institute of Petroleum Processing RIPP), 2009
 - 15 Mueller B, van Langeveld A D, Moulijn J A, Knoezinger H. *J Phys Chem*, 1993, **97**: 9028
 - 16 Shimada H. *Catal Today*, 2003, **86**: 17
 - 17 Hensen E J M, Kooyman P J, van der Meer Y, van der Kraan A M, de Beer V H J, van Veen J A R, van Santen R A. *J Catal*, 2001, **199**: 224

英 译 文

English Text

Al₂O₃ is one of the most promising support because of its abundance and good properties such as high surface area, good pore distribution, and good stability. Al₂O₃ is widely used as the support of hydrotreating catalysts in the petroleum refining industry [1]. The different physiochemical properties of alumina can greatly influence the catalytic activity of the catalysts [2–7]. Domínguez-Crespo et al. [5] found a correlation of particle size of the alumina support with the NiMo oxide catalysts, and the final NiMoS catalyst, and reported that this was important in determining the changes of the active sites during the annealing and sulfidation steps. Sakashita et al. [6,7] investigated the effects of surface orientation and crystallinity of the support on the microstructure of supported Mo catalysts, and showed that the microstructure of the MoS₂ clusters can be controlled by tailoring the surface orientation of the alumina support. However, there is little information available in the literature about the effect of alumina on the formation of the active phase and hydrodesulfurization (HDS) activity and selectivity of the corresponding CoMo catalysts due to the lack of suitable techniques that can directly provide information on the active sites.

The aim of this work is to study the effect of the surface characteristics of two different commercial alumina supports on metal-support interaction and its correlation with HDS activity and selectivity of CoMo catalysts by a variety of techniques, including X-ray diffraction analyses (XRD), Fourier transform infrared spectroscopy (FT-IR), transmis-

sion electron microscopy (TEM), scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX), X-ray photoelectron spectrometer (XPS), and in situ FT-IR of adsorbed CO.

1 Experimental

1.1 Catalyst preparation

Two different commercial alumina, Al₂O₃-1 and Al₂O₃-2, obtained from Changling Division of SINOPEC Catalyst Company, were used without further treatment. Co-Mo/Al₂O₃-1 and Co-Mo/Al₂O₃-2 with the same loading of 2.5% CoO and 8.0% MoO₃, were prepared by the pore volume co-impregnation method with an ammonia solution of cobalt nitrate and ammonium heptamolybdate, followed by drying at 393 K for 2 h and calcination at 693 K for 4 h.

1.2 Catalyst characterization

The sample used for FT-IR was pressed into a self-supporting wafer and placed in an infrared cell. The sample was degassed at 673 K for 4 h. Surface hydroxyl groups on the alumina were determined at 373 K on a Nicolet 6700 Fourier transform infrared spectrometer. Support acidity was determined after the same surface pretreatment. Pyridine was introduced into the cell at 373 K. After adsorption for 15 min, the sample was evacuated at 473 K and 623 K, and the FT-IR spectra were recorded using 64 scans with a resolution of 4 cm⁻¹.

The surface area and pore volume of the samples were determined by N₂ physisorption using a Quantachrome Autosorb-6B automated system.

XRD patterns were recorded in the 2θ = 5°–80° at steps of 0.02°/s on a Philips X'Pert diffractometer using Cu K_α radiation at 0.15418 nm, 40 kV, and 50 mA.

TEM images of the sulfided catalysts were recorded on a Tecnai G² F20 S-TWIN microscope equipped with a STEM unit and a Thermo Noran EDX system. The particle size distribution was determined by counting about 500 particles. The average particle length ($\bar{L}$), stacking number ($\bar{N}$) and stacks per 1000 nm² ($\bar{D}$) were determined by manual measurement and calculated as follows [8]:

$$\begin{aligned}\bar{L} &= \sum_{i=1}^n n_i l_i / \sum_{i=1}^n n_i \\ \bar{N} &= \sum_{i=1}^n n_i N_i / \sum_{i=1}^n n_i \\ \bar{D} &= (n/S) \times 1000\end{aligned}$$

STEM-EDX was used to detect the distribution of the Co and Mo elements. The pretreatment of the sample was the same as used for TEM.

The catalyst was pressed into a self-supported wafer and placed in the IR cell. For the first procedure, the catalyst was

dried at 423 K under N_2 flow for 1 h and was then sulfided with 10% H_2S in H_2 at 673 K. After 5 h, the catalyst was evacuated at 573 K for 3 h and finally cooled down to 100 K using liquid nitrogen. CO adsorption was performed by the introduction of a saturation amount of CO. The spectra of adsorbed CO reported in this study are subtracted spectra, i.e., the spectra of adsorbed CO minus the reference spectrum of the sample before CO adsorption.

The sulfided samples were transported into the preparation chamber of the spectrometer under the protection of argon. The spectra were recorded with a Thermo-Fisher ESCALAB 250 X-ray photoelectron spectrometer using monochromatic 150 W Al K_α radiations. The binding energies were referenced to the Al 2p line at 74.7 eV from the Al_2O_3 carrier. For the deconvolution of the S 2p and Mo 3d peaks, the following constraints were imposed: the spin-orbit splitting of the S 2p and Mo 3d peaks were fixed to be 1.15–1.18 and 3.15–3.20, respectively. The area ratios of S 2p and Mo 3d peaks were equal to the theoretical values of 2.0 and 1.5, respectively.

1.3 Catalytic activity evaluation

The catalysts were presulfided in situ with a sulfiding feed of 6 vol% CS_2 in cyclohexane at a pressure of 1.6 MPa and temperature of 593 K for 3 h. The catalytic activity tests were carried out in a continuous flow-fixed bed microreactor under the following conditions: 1.6 MPa, 533 K, 1.00 g catalyst used, 10% thiophene and 20% 1-hexene in heptane as feed at the feed flow rate of 0.16 ml/min, and a H_2 flow rate of 360 ml/min. After steady state conditions were reached, the liquid effluent was periodically auto-sampled and analyzed on-line by an Agilent 6890N gas chromatograph. The HDS activity (X_T), hydrogenation activity (X_H) and HDS selectivity factor (S) of the catalysts were calculated as follows [9]: $X_T = [(w_{T,1} - w_{T,2})/w_{T,1}]$, $X_H = [(w_{H,1} - w_{H,2})/w_{H,1}]$, $S = \ln(1 - X_T)/\ln(1 - X_H)$. Where $w_{T,1}$ and $w_{T,2}$ denote the thiophene content in the feed and products, respectively. $w_{H,1}$ and $w_{H,2}$ denote the hexene content in the feed and products, respectively.

2 Results and discussion

2.1 Distributions of hydroxyl group and acid site on the supports and their effect on the dispersion of the active metal component

The FT-IR spectra of the hydroxyl groups on the two alumina supports are presented in Fig. 1(a). The hydroxyl group amount of Al_2O_3 -2 was notably less than that of Al_2O_3 -1. The nature and concentration of the hydroxyl group can play an important role in the dispersion of the supported

metal species. The deposition of the catalytically active components on the supports led to a strong decrease of the intensity of the band due to the hydroxyl groups, indicating that the hydroxyl groups were involved in the interaction with the metal precursors and the dispersion of the active metal species [10]. Therefore, as compared with Al_2O_3 -1, there will be a weaker interaction between the metal species and Al_2O_3 -2. This would benefit the sulfidation of the metal component supported on Al_2O_3 -2 and formation of the sulfided active phase.

The FT-IR spectra of the chemisorbed pyridine were used to investigate the distribution of L and B acid sites on the support. Figure 1(b) shows the spectra after adsorption of pyridine on the support. The surface acid amounts of the two supports are presented in Table 1. There were only L acid sites on the two alumina supports at the two different temperatures. The results also showed that the amount of L acid site of Al_2O_3 -1 was more than that of Al_2O_3 -2. This indicated that fewer electron vacancy sites existed on Al_2O_3 -2 than on Al_2O_3 -1, which would lead to a weaker interaction between the active metal component and Al_2O_3 -2.

To investigate the effect of the support on metal dispersion, the STEM-EDX technique was used to observe the distribution of the Co and Mo elements on the support surface. The results are given in Fig. 2. It is clear that the distributions of the Co and Mo elements on the surface of Al_2O_3 -2 supported catalyst were more even than those on the Al_2O_3 -1 supported counterpart.

2.2 Textural properties and phase analysis

The textural properties of the samples are listed in Table 2, which shows that the surface area and pore volume of Al_2O_3 -2 and Co-Mo/ Al_2O_3 -2 were smaller than those of Al_2O_3 -1 and Co-Mo/ Al_2O_3 -1, respectively. It was also observed that the surface properties of Co-Mo/ Al_2O_3 -1 and Co-Mo/ Al_2O_3 -2 catalysts were very similar to those of the Al_2O_3 -1 and Al_2O_3 -2 supports, respectively.

The XRD patterns in Fig. 3 showed that Al_2O_3 -1 and Al_2O_3 -2 were both pure γ -phase (PDF 48-367), but Al_2O_3 -2 has better crystallinity, which was shown by the higher intensity and narrower diffraction peak. After the loading of Co and Mo, no obvious peaks of metal oxides were observed in the XRD patterns of Co-Mo/ Al_2O_3 -1, but a small peak at $2\theta = 26.5^\circ$, characteristic of β -CoMoO₄ (PDF 21-868), was found in the XRD patterns of Co-Mo/ Al_2O_3 -2. This indicated that the Co and Mo species have a better interaction with Al_2O_3 -2 than with Al_2O_3 -1. It is suggested that this was due to fewer hydroxyl groups being present on the surface of well-crystallized Al_2O_3 -2 and the weaker interaction between the active phase and Al_2O_3 -2 in Co-Mo/ Al_2O_3 -2.

2.3 Active phase distributions of sulfided catalysts

Representative TEM micrographs of sulfided Co-Mo/Al₂O₃-1 and Co-Mo/Al₂O₃-2 are shown in Fig. 4. The photos show the well-known MoS₂ slab-like structure. The average slab length, stacking number, and slab number per 1000 nm² of the sulfided catalysts are summarized in Table 3. There was a remarkable increase of the average slab length (from 4.2 to 5.6 nm) and stacking number (from 1.6 to 2.3 nm) on sulfided Co-Mo/Al₂O₃-2 as compared with sulfided Co-Mo/Al₂O₃-1. This can be attributed to the weaker metal-support interaction for Co-Mo/Al₂O₃-2. It has been reported that an increased stacking layer of a sulfided catalyst can weaken in part the polarization of the aluminum ions on alumina surface, and exert a promoting effect of cobalt on molybdenum to form more of the CoMoS active phase.

2.4 XPS results of sulfided catalysts

The Mo 3*d* and S 2*p* XPS spectra for the sulfided Co-Mo/Al₂O₃ catalysts are presented in Fig. 5. Their peak positions are listed in Table 4. These results are close to those reported previously [11,12]. The doublet of 228.8 and 232.0 eV is characteristic of the sulfided Mo⁴⁺ species. This indicated that Mo was mainly in the form of Mo⁴⁺. Two relatively small peaks at about 232.4 and 235.8 eV was attributed to unsulfided Mo⁶⁺. The peaks at 230.3 and 233.6 eV indicated a Mo⁵⁺ species, an intermediate oxidation S-Mo-O state. The binding energy regions of the Mo 3*d* and S 2*s* peaks overlap. Therefore, the influence of the S 2*s* peak must first be ruled out to get the true intensity of the Mo 3*d* peak. The peaks located at 161.7 and 164.7 eV corresponded to S²⁻ and a small fraction of terminal S₂²⁻. The peak of 163.6 eV can be assigned to bridging S₂²⁻ and oxysulfide sulfur. The absence of a signal at 169.0 eV, which is that of sulfate species, indicated there was no oxidation of the catalysts during transfer from the sulfidation reactor to the XPS spectrometer. It can be seen that the support did not affect the binding energies of the Mo species in the sulfided Co-Mo/Al₂O₃ catalysts, which indicated that the type of Mo species present did not depend on the support. However, the support affected the relative amounts of the different chemical states.

The XPS intensity ratios of different chemical states of the main elements in the sulfided catalysts were calculated from the result of XPS peak fitting. The corresponding XPS intensity ratios for the sulfided catalysts are listed in Table 4. The sulfidation extent of Mo was determined by using the fraction of Mo⁴⁺ species in the total Mo species $n(\text{Mo}^{4+})/n(\text{Mo})$. It can be seen that the sulfidation extent of the Mo phase of Co-Mo/Al₂O₃-2 was higher than that of Co-Mo/Al₂O₃-1. The $n(\text{Mo}^{6+})/n(\text{Mo})$ ratio was significantly lower on Co-Mo/Al₂O₃-2 than on Co-Mo/Al₂O₃-1 suggesting a de-

crease of unsulfided Mo species and interaction between metal species and support on Co-Mo/Al₂O₃-2. This was consistent with the FT-IR and TEM results. It should be noted that the Co 2*p* XPS peaks were not deconvoluted because the Co 2*p* XPS signals were weak. Table 4 shows only the dispersion of total Co on the support ($n(\text{Co})/n(\text{Al})$). It can be seen from Table 4 that $n(\text{Co})/n(\text{Al})$ was higher on Co-Mo/Al₂O₃-2 than on the Co-Mo/Al₂O₃-1.

2.5 Distribution of active phase from in situ FT-IR

Figure 6 shows the behavior of CO adsorbed on the sulfided Co-Mo/Al₂O₃ with different supports. Five main bands were observed at 2191, 2153, 2108, 2069, and 2051 cm⁻¹, respectively, which were assigned to CO coordinated to Lewis acid sites (Al³⁺), CO hydrogen-bonded to acidic hydroxyl groups (Brönsted acid sites of the support), CO adsorbed on unpromoted Mo sites that are 6-fold coordinated Mo centers, CO in interaction with 5-fold and 4-fold coordinated Mo atoms adjacent to a Co atom, namely, CO adsorbed on CoMoS [13].

To analyze the effect of the support on the formation of unpromoted and Co-promoted sites quantitatively, the FT-IR spectra were deconvoluted. The CO spectra in the range of 1925–2250 cm⁻¹ were decomposed into several components corresponding to interactions with Al³⁺, OH, unpromoted Mo sites, and three kinds of Co-promoted Mo (CoMoS) sites as well as due to physical adsorption [14,15]. A typical deconvolution of an FT-IR spectrum is illustrated in Fig. 6. The concentrations of the Co-promoted sites were taken to be the sum of the intensities of three CO-CoMoS bands. The degree of promotion of the catalyst can be characterized by the intensity ratio of the bands of CO adsorbed on CoMoS (CO-CoMoS) to those on MoS₂ sites (CO-MoS₂). It should be noted that there was a remarkable increase in the CO-CoMoS integral area (from 5.6 to 6.2) and $A(\text{CO-CoMoS})/A(\text{CO-MoS}_2)$ (from 4.03 to 8.33) of sulfided Co-Mo/Al₂O₃-2 compared with those of sulfided Co-Mo/Al₂O₃-1. This indicated that Co and Mo species were able to form more of the CoMoS active phase on Co-Mo/Al₂O₃-2, resulting in improvement of HDS activity and selectivity.

2.6 HDS activity of the catalysts

The results of the HDS of thiophene are given in Table 5. As compared with Co-Mo/Al₂O₃-1, Co-Mo/Al₂O₃-2 gave a higher conversion of thiophene, but the HYD activities of the two catalysts were roughly the same. A remarkable enhancement in HDS selectivity by Co-Mo/Al₂O₃-2 can be observed. It is clear that from the above characterization results that well-crystallized Al₂O₃-2 has less hydroxyl

groups on its surface, which effectively weakened the metal-support interaction and led to the formation of more CoMoS species. The increased stacking layers of sulfided Co-Mo/ Al_2O_3 -2 can shield the polarization of the aluminum ions of alumina to some extent [16,17], which would benefit the promoting effect of Co on Mo, and cause an increase in the formation of CoMoS species and the HDS activity and selectivity.

3 Conclusions

The surface characteristics of two different commercial alumina supports and their effects on metal-support interaction and the relationship with HDS activity and selectivity of

the Co-Mo supported catalysts were studied by means of a variety of techniques. Al_2O_3 -2 with higher crystallinity and fewer hydroxyl groups has a more moderate metal-support interaction, which improved the sulfidation of the molybdenum species, and caused a higher stacking number and longer average slab length for corresponding Co-Mo catalyst. It stimulate the more CoMoS active sites and a higher $A(\text{CO-CoMoS})/A(\text{CO-MoS}_2)$ ratio on Co-Mo/ Al_2O_3 -2 than Co-Mo/ Al_2O_3 -1. Therefore, Co-Mo/ Al_2O_3 -2 exhibit higher HDS activity and selectivity.

Full-text paper available online at ScienceDirect

<http://www.sciencedirect.com/science/journal/18722067>