V- Mo Based catalysts for Oxidative Desulfurization of diesel fuel

Omar Gonzalez-Garcia, Luis Cedeño-Caero*
UNICAT, Facultad de Química, Universidad Nacional Autónoma de México.
Cd. Universitaria 04510 México D.F.
* caero@unam.mx

Introduction

Refiners are facing the challenge of producing cleaner fuels [1-2]. Actual desulfurization process is hydrodesulfurization (HDS), efficient in removing thiols, sulfides, and disulfides, but less effective for thiophenes and thiophene derivatives. Thus, the sulfur compounds that remain in transportation fuels are mainly benzothiophene (BT), dibenzothiophene (DBT), and their alkylated derivatives (DBT with methyl groups at the 4 and 6-positions). HDS is achieved by catalytic processes operated at elevated temperatures (>300°C) and pressures (20–100 atm H_2) using Co–Mo/Al_2O_3 or Ni–Mo/Al_2O_3 catalyst. Through HDS process would be complicated to get to the finish, improvements in size reactor and severe conditions of operation would be needed. The oxidesulfurization (ODS), is an excellent option after HDS process since the difficult-to-hydrodesulfurize refractory substituted dibenzothiophenes (DBTs), are easily oxidized under low temperature and pressure conditions to form the corresponding sulfones [3].

In order to approach a continuous ODS process, V-based catalysts and V-Mo catalysts have been tested during several reactive-batch cycles and used as reference of spent HDS catalysts (SCH) deactivated with vanadium. These spent catalysts contain mainly Mo, Ni and V oxide species on alumina, so they can be used as ODS catalysts [4]. Finally, as changes in V oxidation state are most likely happening during ODS process, reduced VOx phases were evaluated to explain how catalyst acts in front of oxidant.

Materials and Methods

Hexadecane was used as solvent of model compounds: dibenzothiophene, 4-methyl dibenzothiophene and 4,6-dimethyl dibenzothiophene. This model diesel was prepared with 610 ppm total S. Commercial Mexican-diesel fuel had 350 ppm of total S. Acetonitrile was used as extraction solvent. Hydrogen peroxide (30 wt.% H_2O_2) and tert-butyl peroxide (70 wt.% TBHP) were used as oxidant agents.

V-Mo oxides were supported on pellets (gamma-alumina), prepared by the wet-impregnation method and SCH were used after adequate re-activation. All catalysts were characterized by X-ray, textural properties (obtained by N_2 adsorption-desorption isotherms of the samples) and elemental composition was determined by SEM-EDX elemental analysis system.

All ODS cycles were performed in a glass batch reactor (immersed in a thermostatically controlled water bath), fitted with condenser, mechanical stirrer and a thermocouple. An ODS reactive cycle lasts 60 minutes, containing mixture diesel-solvent (1:1 vol. ratio), oxidant agent (initial O/S molar ratio of 13) and catalyst (pellet). Then, spent solutions (diesel and solvent) are removed and fresh solutions are added to perform a new reactive cycle. After each ODS cycle, samples of diesel and solvent phases were withdrawn and injected (auto sampler) to the GC-FID and/or GC-PFPD for quantitative analysis.

Results and Discussion

Performance of all catalysts qualitatively is similar, during ODS cycles; with H_2O_2 as oxidant, deactivation was observed (Fig. 1 A), whereas with TBHP catalysts do not suffer deactivation and an increase in sulfone yield was observed during ODS cycles (Fig. 1 B, C and D). By initial incorporation or decomposition of oxidant, water produced deactivation, but there are others factors, like presence of reduced VOx, that make important effects increasing sulfone yield, more significantly for TBHP. Reduced catalysts of V-Mo/A (obtained in a conventional TPR apparatus) were prepared and tested in ODS cycles. Results of sulfone yields of DBTs using TBHP, showed similar trends to those obtained with original-oxide catalysts. But, if catalyst is reduced sulfone yields are appreciably higher (Fig. 1 C). SCH show similar trends, in figure 1 D we can see an activation during ODS cycles with TBHP, this gives rise that during the reaction, active phases in catalysts rearrange to a phase that are not fully oxidized.

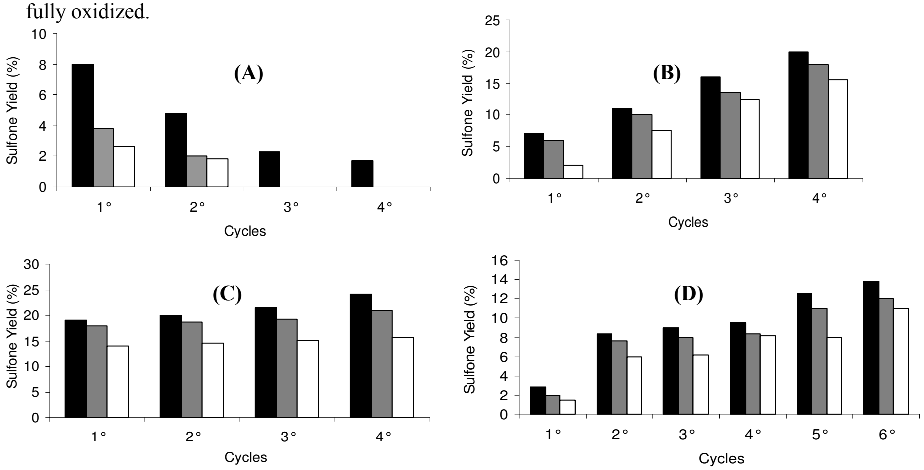

Figure 1. Sulfone yield of DBT (■), 4-MDBT (▨) and 4,6-DMDBT (□): using V-Mo/A with (A) H_2O_2 or (B) TBHP. (C) Using reduced V-Mo/A and TBHP. (D) Using SCH and TBHP.

Significance

ODS could be the next stage after HDS, using spent catalysts of hydroprocessing (after adequate activation) to mild conditions of operation. It is important to understand ODS process in order to give it to petroleum refining industry and to produce ultra low sulfur fuels.

References

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