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IR study of the interaction of phenol with oxides and sulfided CoMo catalysts for bio-fuel hydrodeoxygenation

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ABSTRACT

The adsorption of phenol on supported sulfide CoMo catalysts and on oxides is investigated using IR spectroscopy. On silica, phenol mainly interacts via hydrogen-bonding, whereas on alumina it dissociates on the acid–base pairs of this oxide leading to the formation of strongly adsorbed phenolates species. On a sulfided CoMo catalyst supported on alumina, phenol dissociates on the support but does not interact strongly with the sulfide phase. The accessibility of the various sites of the catalyst after phenol contact is investigated by CO adsorption monitored by IR spectroscopy. As expected, phenolate formation decreases the accessibility of support sites. In addition, a decrease of the sulfide site accessibility is also observed. This is indicative of an indirect poisoning of the sulfide edge sites by phenolate species anchored on the support and in the vicinity of sulfide slabs. Consequently, decreasing the amount or strength of the acid–base paired sites of the support should be a way to limit deactivation.

1. Introduction

In order to develop sustainable transportation fuels, the contribution of biomass derived feedstocks is set to grow above today's levels. For ethical reasons, the use of raw materials not competing with the food production chain should be the most preferred route. One option is to produce biofuels by pyrolysis of organic waste and lignocellulosic plant material (i.e. second generation biomass). Since these pyrolytic oils contain very large quantities of oxygenated compounds (up to 40 wt% O), their hydrodeoxygenation (HDO) is a way to produce stable fuels [1,2]. Hydroprocessing catalysts like the supported sulfided ((Co,Ni)Mo) catalysts used in the hydrodesulfurization (HDS) of oil fractions could be good candidates if their deactivation can be limited under HDO conditions [3–8]. The high concentration of phenolic compounds found in pyrolytic oils (2–20 wt%) was related to the fast deactivation observed during their HDO on the supported sulfided catalysts used in pioneering studies [3]. Our goal is to identify the cause of catalyst deactivation during HDO of phenolic compounds in order to better define the design rules of effective HDO catalysts.

We report the use of infrared (IR) spectroscopy to determine the adsorption modes of phenol on (i) oxides with different acid–base properties like alumina and silica, they are the supports commonly proposed for hydroprocessing catalysts, (ii) alumina supported sulfided CoMo catalysts. In addition, the accessibility of the catalysts sites after phenol adsorption is monitored by IR spectroscopy of adsorbed CO.

2. Experimental

2.1. Materials

The silica sample is an Ultrasil 7000 (from Evonik) with a surface area of 173 $m^2 g^{-1}$. The alumina is a CatapalC (from Grace Davison) with a surface area of 292 $m^2 g^{-1}$. The CoMo/Al_2O_3 catalyst (9.2%Mo to 4.2% Co) is prepared by a classical impregnation using heptamolybdate ammonium and cobalt nitrate deposition on alumina (from Sasol) with a surface area of 255 $m^2 g^{-1}$. Phenol is supplied by Prolabo (purity 99.5%).

2.2. Infrared spectroscopy

Each sample is pressed into a self-supported disc (~10 mg, 2 cm^2). The disc is introduced in the infrared cell for in situ sulfidation. The sample is first dried under an Ar flow (30 ml/min) for 0.5 h at 423 K and, then cooled down to 298 K. The catalyst is then sulfided under an H_2S (10%)/H_2 (30 ml/min) flow up to 623 K (ramp of 3 K/min). After 1 h of sulfidation at 623 K, the sample is evacuated at the same temperature.

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After activation in the IR cell, calibrated doses (from 0.015 μmol to 0.775 μmol) of phenol are introduced stepwise on the oxides and the sulfide catalyst. The final equilibrium pressure in the infrared cell is set to 20 Pa. Afterwards, the cell is evacuated at 298 K for 15 min. In another set of experiments, a phenol pressure of 20 Pa is introduced directly on the samples at 623 K, followed by evacuation at the same temperature for 15 min.

In order to evaluate the interaction of phenol with the sulfide phase, CO is adsorbed before and after phenol introduction. Again, calibrated doses of CO are introduced on the sample, at ~100 K, followed by a desorption stage from 100 K up to 298 K.

The infrared spectra are recorded with a FT-IR spectrometer Nicolet Magna AEM equipped with a MCT detector (64 scans, resolution 4 cm^{-1}, “zero filling” 1 level). All the spectra are normalized to a mass of 5 mg cm^{-2}.

3. Results and discussion

3.1. Phenol adsorption on silica

Fig. 1 shows the adsorption of phenol on silica at 298 K (spectrum a). Table 1 reports assignments based on work reported elsewhere [9,10]. The adsorption of phenol on silica leads to bands at 1599 cm^{-1} (with a shoulder at ~1606 cm^{-1}) and 1500 cm^{-1} assigned to ν(CC) ring vibrations. Bands at 1474 and 1360 cm^{-1} contain a significant contribution of δ(OH) vibration (~20%). Note that the band at 1474 cm^{-1} is generally attributed to ν(CC) ring vibrations [9,10]. However, this mode includes a δ(OH) contribution (~15%), also observed (not shown) on the spectra recorded with deuterated phenol (OD position). These characteristic δ(OH) vibrations highlight the presence of molecular phenol. After evacuation at 373 K (spectrum b), an important part of the perturbed SiO–H bands disappears along with those at 1474 and 1360 cm^{-1}. However, the bands characteristic of ν(CC) ring vibrations at 1599 cm^{-1} and 1496 cm^{-1} remain. They are still present even after evacuation at 673–723 K (spectrum c). The νOH region of silica shows that the band at 3745 cm^{-1} (silanol groups) shifts to lower wavenumbers, giving rise to two broad components at 3620 and 3490 cm^{-1}. Evacuation at 373 K almost completely removes, these perturbed SiOH groups.

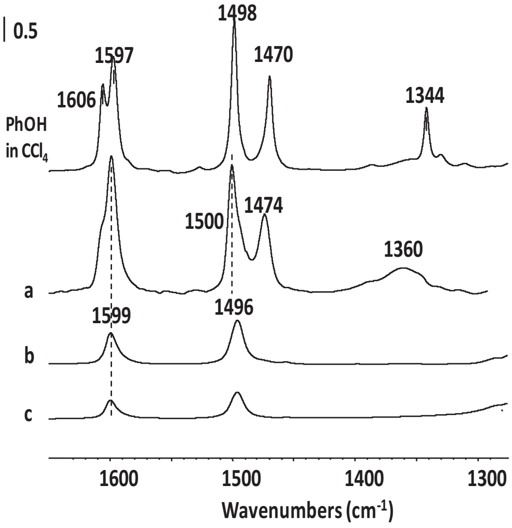

Fig. 1. Infrared spectra of phenol adsorbed on silica. Equilibrium pressure of 20 Pa at room temperature (a); after evacuation at 373 K (b), and 673 K (c). Comparison with phenol in CCl$_4$.

Table 1
Assignments of the IR bands of liquid phenol.

Assignment	Phenol
ν(OH)	3610
ν(CHring)	3074–3021
ν(CH3)	–
ν(CCring)	1608
ν(CCring)	1600
ν(CCring)	1502
ν(CCring) + δ(OH)[a]	1473[a]
δ(CH3)	–
ν(CCring) + δ(OH), polymer	1362
ν(CCring) + δ(OH), monomer	1344
X-sensitive (ν(CCring) + ν(CO))	1259

[a] Assignment based on experiments with deuterated molecules.

The IR spectrum of phenol absorbed on silica indicates a hydrogen bonded interaction (Fig. 1). This is substantiated by: (i) the presence of phenol δ(OH) bands and the shift of the 1344 cm^{-1} band to 1360 cm^{-1} with a broadening and splitting into several components, (ii) a decrease of the SiOH band intensity with the appearance of several new bands corresponding to perturbed SiOH bands, (iii) the restoration of a significant fraction of the silanol band after evacuation at 373 K. In conclusion, at room temperature, the predominant adsorption mode of phenol on silica is hydrogen bonding.

3.2. Phenol adsorption on alumina

The infrared spectrum of phenol adsorbed on alumina (Fig. 2a) presents bands at ~1597, 1498/1492 cm^{-1}, characteristic of aromatic ring vibrations. For small amounts of phenol adsorbed (not presented here), the δ(OH) bands at ~1470 and ~1340 cm^{-1} are not observed. With increasing phenol coverage, only a shoulder appears at ~1470 cm^{-1} (spectrum a) and disappears after evacuation at 373 K (spectrum b). A multi-component ν(CO) broad band (1300 to 1230 cm^{-1}) develops also [2,3]. These observations are similar for the two alumina sources (Grace Davison and Sasol).

Fig. 2 shows that the interaction of phenol with alumina leads to the formation of phenolate species. Indeed, bands corresponding to aromatic rings (1597 and 1498/1492 cm^{-1}), and to ν(CO) vibrations (1295/1250 cm^{-1}) appear, while those characteristic of δ(OH) groups (at ~1470 and ~1340 cm^{-1}) are absent, except at high coverage and with a very low intensity (spectrum a). The presence of two different components in the ν(CO) band (1498/1492 and 1295/1250 cm^{-1}) suggests the formation of two phenolates, mono-and bi-dentate, as illustrated in Fig. 3.

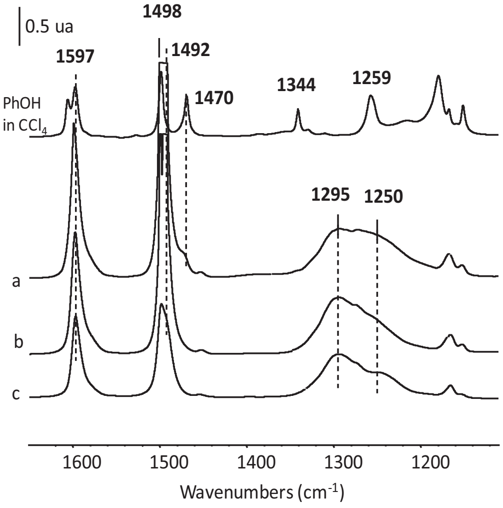

Fig. 2. Infrared spectra of phenol adsorbed on alumina. Equilibrium pressure of 20 Pa at room temperature (a); after evacuation at 373 K (b), and 673 K (c). Comparison with phenol in CCl$_4$.

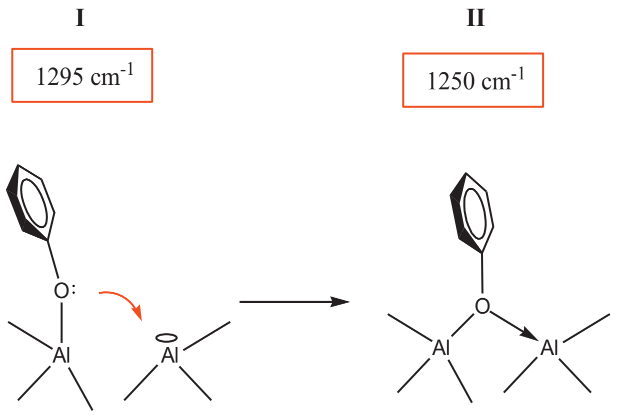

Fig. 3. Structure of phenolates species on alumina.

3.3. Phenol adsorption on a sulfided catalyst

Phenol was adsorbed on sulfided CoMo/Al_2O_3 at 623 K (Fig. 4). The spectra display the same main bands positioned at 1597 cm^{-1}, 1498/1492 cm^{-1} (ν(CC) ring vibrations) and 1296/1245 cm^{-1} (ν(CO) vibrations) as observed on alumina alone. The absence of bands at ~1470 and ~1340 cm^{-1}, characteristic of a δ(OH) vibration, indicates the formation of phenolate species on alumina alone. Moreover, the normalization of the spectra to the most intense band (see Fig. 4 insert) confirms the similarity in the ν(CO) region between the two samples. This indicates that there is no structural difference between the phenolate species formed on sulfided CoMo/Al_2O_3 and on pure alumina. However, the adsorption bands of phenol are clearly less intense (about 30–40%) on the sulfided CoMo/Al_2O_3 catalyst than on pure alumina. This implies that the phenolate species on the sulfided catalyst are located on the fraction of alumina support not covered by the sulfided phase and not on the sulfide phase, as described in Fig. 5. Two additional shoulders at 1564 and 1450 cm^{-1}, not present on alumina alone, appear on the sulfided CoMo/Al_2O_3 catalysts. They are absent after phenol adsorption at RT on the sulfided catalyst and indicate that phenol reacts with the sulfide phase at high temperature.

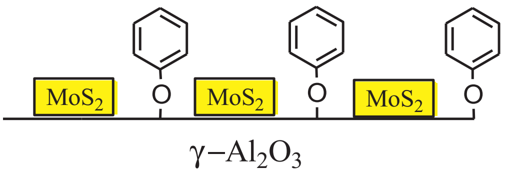

Fig. 5. Phenol interaction on sulfided CoMo/Al_2O_3.

3.4. Phenol and CO co-adsorption on the sulfided catalyst

On sulfided CoMo/Al_2O_3, CO adsorption is characterized by bands at 2188, 2156, 2110, 2070 and 2055 cm^{-1} (Fig. 6). The band at 2188 cm^{-1} corresponds to the interaction of CO with Lewis acid sites of alumina (LAS – Al^{3+}) and the one at 2156 cm^{-1} to its interaction with hydroxyl groups. The other bands characterize the sulfide phase. The one at 2110 cm^{-1} is due to the adsorption of CO on non-promoted Mo sites, while those at 2070 and 2055 cm^{-1} belong to CO on Co promoted sites [11].

CO adsorption on sulfided catalysts in interaction with phenol shows a significant decrease in the accessibility of the support sites. The intensity decrease of the band of CO adsorbed on LAS is expected, since the formation of phenolates on alumina involves Al^{3+} sites. In addition, phenolate formation on the alumina support should indirectly perturb OH groups and therefore limit the interaction CO/OH (decrease of the band at 2110 cm^{-1}).

The IR spectra also show a decrease in the accessibility of the sulfide phase: both bands characteristic of CO adsorption on Co-promoted and unpromoted sulfide sites decrease. Since the analysis of the spectra does not indicate any interaction of phenol with sulfide phase (Fig. 4), we propose that the presence of phenolate species in the vicinity of the support prevents the access of CO to the sulfide phase sites. The carbonaceous species, formed in addition to the phenolates species, in the static conditions reported here should not be considered as poisons because they are not detected

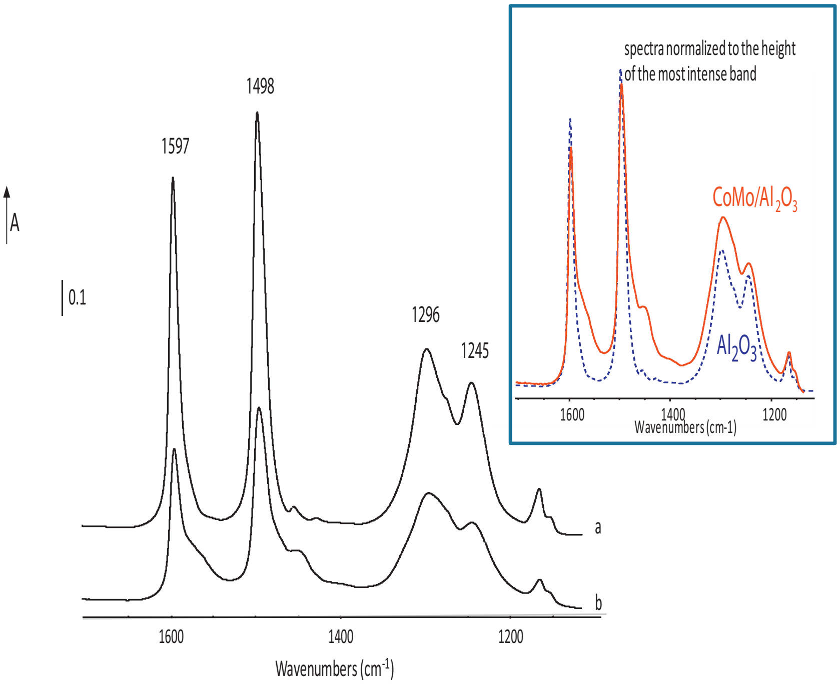

Fig. 4. Infrared spectra of phenol adsorbed on alumina (a) and sulfided CoMo/Al_2O_3 (b) after adsorption of 20 Pa of phenol followed by evacuation at 673 K.

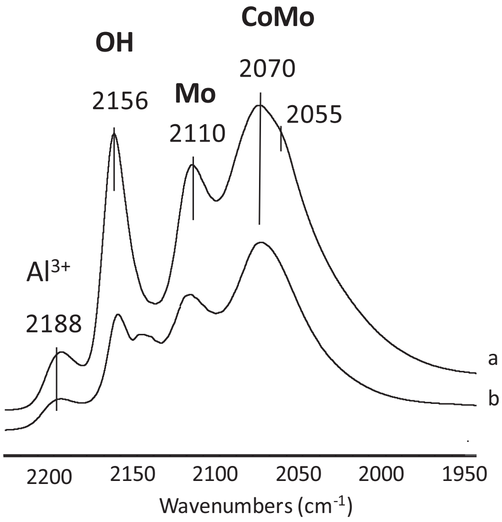

Fig. 6. Infrared spectra of CO adsorbed on sulfided CoMo/Al_2O_3, before adsorption of phenol (a), and after adsorption and desorption of phenol at 623 K (b).

on used catalysts tested under flow conditions of HDO of model molecules [12].

4. Conclusion

The adsorption mode of phenol on oxides such as silica or alumina is related to their acid–base properties. On silica, phenol interacts mainly via hydrogen-bonding, whereas on alumina it dissociates on acid–base pairs leading to the formation of strongly adsorbed phenolates species. On a sulfided CoMo catalyst supported on alumina, phenol dissociates on the support but does not strongly interact with the sulfide phase. As expected, the accessibility of support sites is decreased after phenol adsorption. Moreover, a decrease of the accessibility of the sulfide sites is also observed; it is accounted by an indirect poisoning of the sulfide edge sites by phenolate species anchored on the support and in the close vicinity of sulfide slabs. As a practical consequence, a modulation (i.e. decrease) of the amount or strength of the acid–base pairs of the alumina support could be a way to limit deactivation by phenol. Recent results obtained using more complex phenolic compounds such as guaiacol, lead to similar conclusions [12]. This study is one of the first steps in the rational design of more efficient and stable HDO catalysts of pyrolytic oils. However, each step from a fundamental understanding of materials to a working catalyst with real feedstocks should be monitored by catalytic testing with model and synthetic feedstocks in order to validate the pertinence of all spectroscopic characterizations.

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