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Journal of Catalysis 242 (2006) 16–25

JOURNAL OF CATALYSIS

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An operando Raman study of structure and reactivity of alumina-supported molybdenum oxide catalysts for the oxidative dehydrogenation of ethane

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Received 16 December 2005; revised 12 May 2006; accepted 22 May 2006

Abstract

The structural and catalytic properties of supported MoO_3/Al_2O_3 catalysts with Mo surface densities, n_s, in the range 1.1–12.5 Mo/nm^2 were studied for the oxidative dehydrogenation of ethane by in situ Raman spectroscopy with simultaneous catalytic measurements at temperatures of 400–550 °C. Isolated mono-molybdates (MoO_4) and polymolybdates are formed at various proportions (depending on the loading) on the catalyst surface under dehydrated conditions; bulk $Al_2(MoO_4)_3$ crystals are formed at n_s exceeding the monolayer. Under reactive environment (C_2H_6/O_2), the Raman features attributed to Mo=O and Mo–O–Mo modes appear to be perturbed, indicating that surface MoO_x species are reduced to lower valence states. The combined information on catalyst structure under reaction conditions and catalytic data shows a concurrence between the trends for activity per Mo (turnover frequency [TOF]) and for the number of Mo–O–Al bonds per Mo as a function of n_s. The catalytic activity is related to the anchoring Mo–O–support bonds. Structure–activity/selectivity relations are derived and discussed.

Keywords: In situ Raman spectra; Ethane ODH; Molecular structure; Molybdena active sites; MoO_3/Al_2O_3 catalysts; Anchoring bonds

1. Introduction

The demand for olefins remains a challenge for the refining and petrochemical industry. The classical commercial processes applied for the production of olefins are energy-intensive, and more economic sources are sought [1,2]. The catalytic dehydrogenation of alkanes is an attractive route for the synthesis of alkenes from the cheaper corresponding alkanes. Both dehydrogenation (DH) [3] and oxidative dehydrogenation (ODH) [4–7] reactions can be used, with often-comparable yields in olefins and losses in CO_x. In the presence of an oxidant (e.g., O_2), the process becomes exothermic, which can result in a control of carbon deposition that would otherwise necessitate frequent catalyst regeneration. However, combustion pathways to CO_x limit alkene yields, especially at high alkane conversions. Therefore, the design of selective catalysts appears critical for the efficiency of the ODH process.

Supported MoO_3 catalysts are important catalytic systems for the oxidative dehydrogenation of light alkanes [8–10]. The efficient activation of the reactants is related to the local structure, the distribution of metal oxide species on the support surface, and parameters related to the preparation procedures of the catalysts [11–13].

Raman spectroscopy is among the most powerful tools for studying catalytic materials and surfaces under in situ conditions [14–19]. It can provide information on the molecular structure of the surface metal oxide species by probing the vibrational properties of metal–oxygen bonds. The structures of MoO_3-supported catalysts at dehydrated conditions evolve from isolated monomers to larger polymolybdates, for submonolayer coverages of the support. For coverages exceeding the monolayer, bulk MoO_3 and/or $Al_2(MoO_4)_3$ crystals have been reported to form on Al_2O_3, depending on the Mo surface density and the sample preparation conditions [20,21]. The relative concentrations of the various surface MoO_x species depend

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0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.05.024

on the specific metal oxide support, the Mo surface density, and the calcination temperature of the sample.

The need for a deeper understanding of the nature and the function of catalytically active species during a catalytic process has led to a dramatic increase in the number of in situ Raman characterization studies [16]. The urge for establishing structure–activity/selectivity relationships has led to the development of spectroscopic instrumentation, allowing monitoring of catalytic systems with simultaneous on-line product analysis under actual reaction conditions. The above strategy has been termed *operando* spectroscopy. Many recent publications have stressed the potential of this strategy and its value in catalysis research [22–26].

This work focuses on the investigation of supported MoO_3/Al_2O_3 catalysts for ethane ODH by means of *operando* Raman spectroscopy. In situ Raman spectra were recorded at temperatures of 400–550 °C with simultaneous collection of catalytic activity data from the same sample. The effect of catalyst composition, temperature, gas atmosphere, and reactant residence time on both Raman spectra and catalytic efficiency was studied. The data were used to derive structure–activity/selectivity relationships for ethane ODH over MoO_3/Al_2O_3-supported catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

Supported MoO_3/Al_2O_3 catalysts were prepared by wet impregnation of γ-Al_2O_3 (Engelhard; surface area [SA] = 183.9 m^2/g). Before impregnation, the support was crushed and sieved to a particle size of 106–180 µm. Ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Fisher] was used as the Mo precursor. To ensure full dissolution of the precursor to water, the solution (0.01–0.06 g/cm^3, pH = 5) was heated at 40 °C. The weight loading of MoO_3 varied between 5 and 30%. Impregnation of the dry alumina particles with the Mo precursor solution was conducted at 70 °C for 1 h in a rotary evaporator. After impregnation, the solvent was removed by evaporation at 70 °C under reduced pressure (200 mmHg) for 45 min. The resulting solid was dried overnight at 120 °C and calcined in synthetic air (flow, 50 cm^3/min) at 650 °C for 6 h in a muffle furnace. The catalysts are denoted by xMoAl, where x indicates the nominal wt% MoO_3 loading of the catalyst.

X-ray crystallography characterization for determining the Mo content, specific SAs, and crystalline phases of the samples has been described elsewhere [8]. The catalyst characteristics are summarized in Table 1.

2.2. In situ Raman spectroscopy with simultaneous gas chromatography analysis

An appropriate homemade in situ Raman cell was designed and constructed for the simultaneous monitoring of Raman spectra and catalytic activity of the studied catalysts (Fig. 1). The reactor cell, which had a gas inlet and a gas outlet as well as an entrance to accommodate a thermocouple sheath, was made of quartz tubing (6 mm o.d.; 4 mm i.d. and 10 mm o.d.; 8 mm i.d. for the central larger part; see Fig. 1) and had

Table 1
Properties of the catalysts

Catalyst	wt% MoO_3		SA	Surface density	Crystalline phases
	Nominal	ICP analysis	(m^2/g)	(Mo/nm^2)	
5MoAl	5	4.8	186	1.1	γ-Al_2O_3
10MoAl	10	9.5	178	2.3	γ-Al_2O_3
15MoAl	15	14.8	161	3.9	γ-Al_2O_3
20MoAl	20	20.3	124	6.7	γ-Al_2O_3, $Al_2(MoO_4)_3$
30MoAl	30	29.3	100	12.5	γ-Al_2O_3, $Al_2(MoO_4)_3$

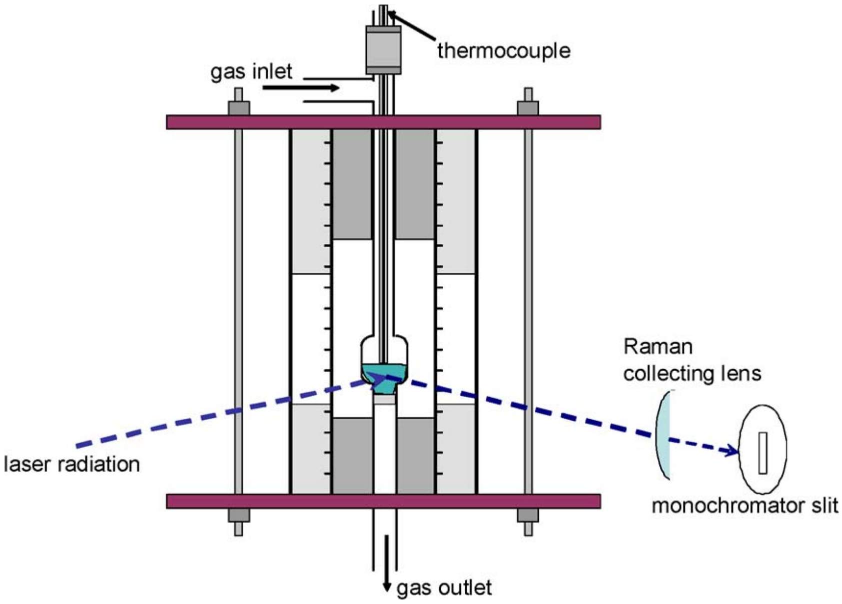

Fig. 1. Home made Raman cell for *operando* Raman—GC measurements.